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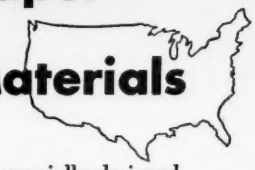

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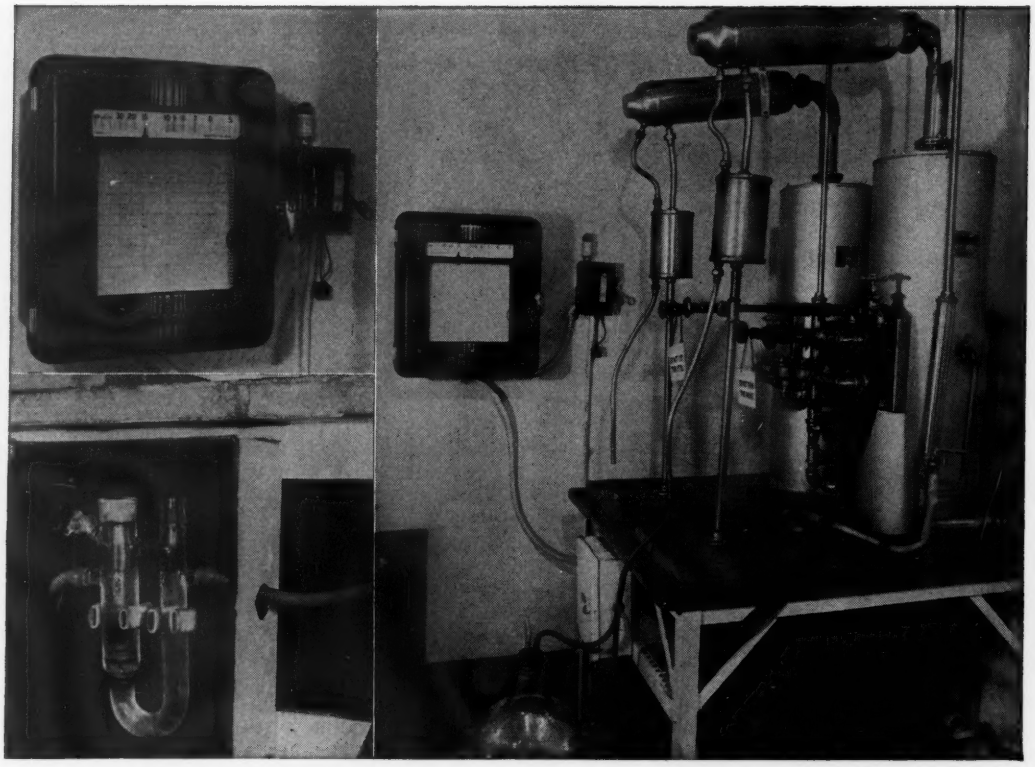

Automatic equipment providing water for intravenous and other parenteral solutions in Jefferson Hospital, Philadelphia. One of the two stills is for standby service. Micromax recorder and cell, which record purity of distillate from still in use, are shown close-up at left.

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Among many interesting features of the Jefferson Hospital centralized sterilization room is an automatic device for checking and recording the purity of distilled water.

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(For further information, see the article, "The History of Nicotine," by Hewitt Grenville Fletcher, Jr., on page 303.)

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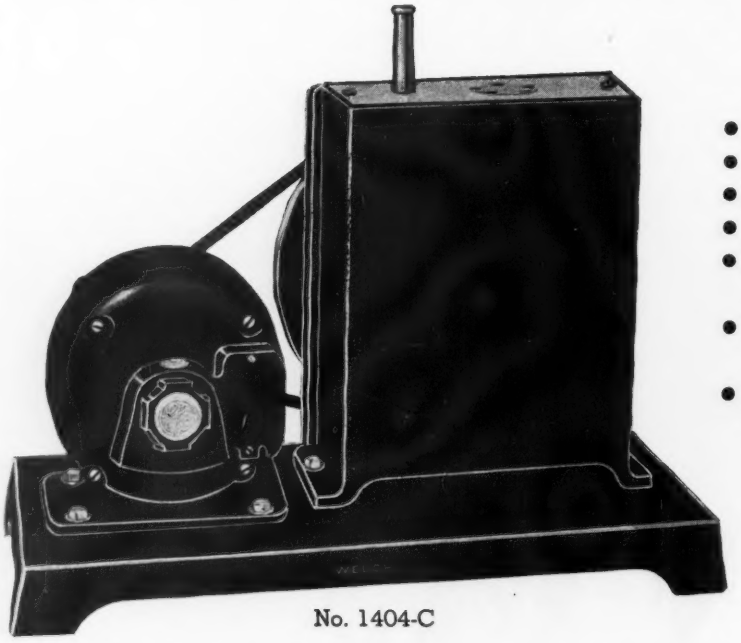

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Editor's Outlook

WE HAVEN'T heard much about the "forgotten man" lately. But there is another we would like to mention who hasn't been forgotten, because we scarcely concerned ourselves about his existence in the first place.

In our constant reminders to young aspirants that "there is always room at the top" we neglect to think about the large number who never get very far in that direction—indeed, are not equipped to do so. Obviously, all education cannot be for leadership; its greater problem is to adapt itself to the capacity of the recipient.

Everyone with the least experience of student or vocational guidance knows how difficult it is to lighten the blow of disillusionment which falls upon most students sooner or later. It is the ideal of our "way of life" to hold out to each and every one the possibility of rising to the highest estate. We know it is a gambler's chance; statistically it is impossible, although the individual may accomplish it. Most of us have to learn to be good losers; sooner or later we come to our limits. But the important thing is that we learn them ourselves; no one else has the right or power to establish them for us.

The chemical profession is a large one, and while the middle ranks are indeed more heavily crowded than the upper ones this is by virtue of both supply and demand. These contain potential leaders, however, who constantly exert pressure on the "higher-ups." But below the middle ranks are those still lower in the scale, the hewers of wood, the drawers of water, the doers-of-the-dirty-work. What relation does chemical education have to these? Considerable, if the numbers involved are any criterion.

Now, with the quickening of the industrial tempo, there will be more openings than ever for young men of limited technical training (although perhaps not of limited capacity) to fill jobs of more or less routine character. Is their supply to be merely a hit-or-miss proposition or can a constructive program be worked out? The high schools will be more or less concerned, since high-school graduates can be used to some extent. Particularly, however, it is a problem over which the junior colleges are worrying. The extent to which these institutions are offering "terminal courses" is perhaps not fully appreciated. They are playing a much more important part in our educational structure in this way than in "feeding" the senior colleges and universities. And the fact is that we have given very little attention to the outlining of a curriculum in chemistry at this level. We will soon have to do so.

We have been defining the profession of chemistry in larger and more technical terms, and rightly. But, whether we like it or not, young men will nevertheless go out from these institutions into industry to do what is obviously chemical work. We must make sure that they are properly equipped for their jobs. How far should their training go, and how should it differ—if at all—from that given in the university?

Still further along is another problem which has had little attention: that of the minor worker in the chemical industry who has had little or no formal training. Some of these have capacity beyond their present positions. Several years ago the Division of Chemical Education established a Committee on Chemical Education of the Non-Collegiate Type. Its report was published—and probably forgotten. But the problem still remains.

A recent communication describing conditions in the chemical profession contained the following:

"In addition to the opportunities evident in the fields of specialized chemistry, industry in particular has considerable need for young men who have had at least a high-school education, for purposes of routine technical control. I know many young men who have worked their way up the ladder to success in plant control laboratories from the humble 'lab boy' to positions that warrant very substantial remuneration."

Education, chemical or otherwise, will always be a process of fitting one as well as possible for the position which he seems destined to occupy, while at the same time giving him a background for the full appreciation of life in general and for further advance to the limit of his inherent capacity.

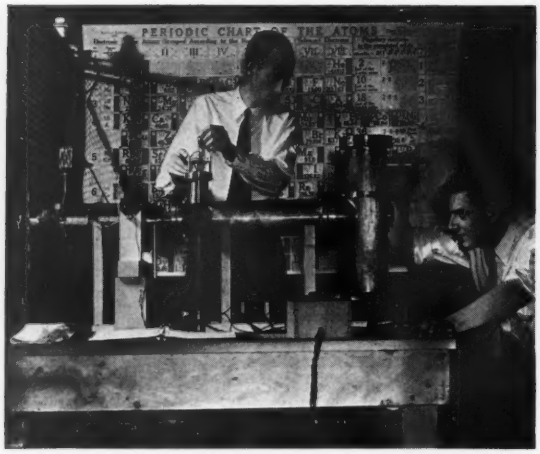
What's Been Going On

Electron Diffraction Camera

AN ELECTRONIC vacuum camera that photographs the crystalline structure of substances millionths of an inch thick has been built by Dr. Ralph P. Johnson of the General Electric Research Laboratory.

The camera is being used to study deposits on the surfaces of metals, *e. g.*, tarnish, polish, lubricants such as grease and oil, and the first stages of corrosion. It supplements X-ray apparatus that permits study of the interior of substances of greater thicknesses.

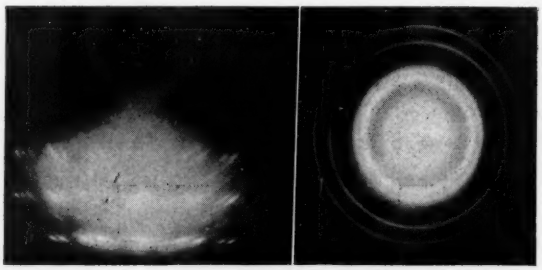
The camera proper consists of a brass tube about three and one-half feet long and a focusing magnet. A 40,000-volt electronic beam enters one end of the tube, is focused by means of the magnet upon the material suspended in the middle of the tube, diffracts, and produces a picture upon a lantern slide at the other end of the tube. The tube is evacuated to permit free passage of the electronic beam without collision with gas molecules. The material to be photographed is suspended in such a way that it can be raised or lowered or tilted at any angle to the beam.



ELECTRON DIFFRACTION CAMERA

Similar cameras have been built by the Bell Telephone Laboratories and others.

The electronic beam is reflected by or transmitted through the material and a diffraction pattern is produced upon the lantern slide. The spacing and intensity of the circles or spots of the pattern enable the physicist to determine the crystalline structure.



(*a*) (*b*)

ELECTRONIC DIFFRACTION PATTERN OF (*a*) SODIUM CHLORIDE AND (*b*) GOLD

IT IS reported in the *Industrial Bulletin* of A. D. Little, Inc., that the Bessemer steel process is taking a new lease on life. Its one main advantage has always been its rapidity—about 18 minutes to "blow" 25 tons of steel, as compared with 10 to 11 hours for the treatment of 150 tons in an open-hearth furnace. But the speed has prevented accurate control and uniformity of product. The end of the blow must be determined with great accuracy to insure success, and this is now being accomplished by means of photoelectric cells.

Another drawback of the Bessemer process has been the impossibility of removing sulfur and phosphorus. Recent improvements have removed this disadvantage. Pretreatment in a ladle with soda ash takes care of most of the sulfur. Phosphorus is removed in a slag, formed by the addition of lime, iron oxide, and fluorspar to the blown metal after pouring.

In 1939 about 3.5 million tons of Bessemer steel were made out of a total of about 53 million tons. This year 15 million out of a possible total of 80 million seems probable.

Another new development reported is the production of a number of new products from the Searles Lake brines. These materials, which represent 40 per cent of the company's tonnage, include soda ash, salt cake, burkeite, bromine and bromides, potassium sulfate, and lithium phosphate. All these except the last are commonly manufactured products, but it is very uncommon to find them as by-products of natural occurrence, as they are in these brines.

EXAMINATION AND TEST CONFERENCE

THE Committee on Examinations and Tests of the American Chemical Society plans to consider the work for the coming two years at a week or ten-day conference at the University of Chicago, beginning July 21, 1941. Particular attention will be given to the newer developments in evaluation, such as the measurement of achievement in the ability to use the scientific method, formulate hypotheses, draw conclusions, interpret data, apply principles, and reason logically in the field of chemistry. The Committee is also concerned with possible methods of measuring accomplishment of the following teacher objectives: development of attitudes, appreciation, and interest in subject matter.

An added attraction at the University during this period are the lectures of Dr. Linus Carl Pauling of the California Institute of Technology.

For further information and for reservations, write to Dr. T. A. Ashford of the University of Chicago or to the Chairman of the Committee, Dr. O. M. Smith, Oklahoma Agricultural and Mechanical College, Stillwater, Oklahoma.

The History of Nicotine

HEWITT GRENVILLE FLETCHER, JR.

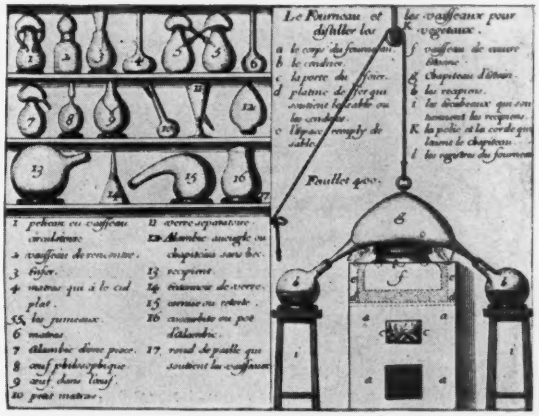
Massachusetts Institute of Technology, Cambridge, Massachusetts

Nicotine, the chief active principle of tobacco, has been known in a more or less pure state almost since the introduction of the plant into Europe in the middle of the sixteenth century. The story of this compound from the first observation of a Paracelsan alchemist to the final synthesis by a modern chemist forms an interesting thread through the history of organic chemistry—a thread which touches the history of pharmacy, the founding of the modern science of toxicology, and some of the most interesting characters of chemical science.

NICOTINE, like so many other naturally occurring substances, was known for centuries in an impure state. The first certain description we have of it was written in 1571, about twenty years after Thevet is said to have introduced the plant into the old world.[1] That this discovery was made so early is not surprising because of three factors. In the first place the sixteenth century witnessed the rapid rise of botany. Botanical gardens were founded in Pisa (1543), Florence (1544), Bologna (1547) and, as we shall later see, in Paris. Herbals began to appear in numbers and medical interest was turned to preparations from plants. Secondly, the period of the first exploration of the new world was one of high hopes for the value of the products which the explorers brought back. Plants of all sorts were imported in great numbers and investigated widely for their medicinal values. Especially exaggerated were the hopes held for the curative value of tobacco. The explorers saw the natives smoking the dried leaves and using the fresh ones to heal their wounds. It was only after about fifty years in Europe that tobacco ceased to be considered simply as an herb and smoking became general. A quotation will serve to illustrate the attitude then prevalent toward the new plant.

> Nicotiane [the plant], although it bee not long since it hath beene knowen in Fraunce, not-withstanding it deserveth Palme and Price emong all other Medicinable herbes, it deserveth to stande in the first rancke, by reason of his singular vertues, and as it were almost to be had in admiration, as hereafter you shall understande.[2]

Lastly, the prevailing method of organic analysis in the sixteenth and seventeenth centuries was that of dry distillation with varying degrees of heat.[3] Although the process of distillation itself may be traced to the Alexandrian chemists, it was only with the beginning of the sixteenth century that the distillation of plants for the preparation of "essences" and medicines



From Le Fèvre's "Traité de la Chymie," Paris, 1660

APPARATUS FOR DISTILLING PLANTS

came into general use. In the year 1500 Hieronymous Brunschwygk of Strassbourg gathered together what were probably the prevailing methods of the physicians of his city and printed them in an extremely handsome and profusely illustrated book entitled, "Liber der arte distillandi de simplicibus" (in German). That Paracelsus, the great Swiss iatrochemist, knew of this work seems likely.[4] At any rate he was very familiar with the processes described therein and used them frequently. In his "De Natura Rerum" we find this passage, the ideas of which persisted in Europe for nearly two centuries:

> The separation of those things that grow from the earth and are easily combustible, as all fruits, herbs, flowers, leaves, grass, roots, wood, etc., takes place in many ways. Thus by distillation is separated from them, first, the phlegm, then the mercury and the oily parts, third, its resin, fourth, its sulfur, and fifth, its salt. When this separation has taken place by chemical art, there are found many splendid and powerful remedies for internal and external use.[5]

[1] See BOWEN, *Isis*, **28,** 351–2 (1938). The exact date of the introduction of tobacco into Europe has been the subject of much research. The consensus of present opinion seems to set it indefinitely near the middle of the sixteenth century.

[2] John Frampton's addition to his translation of Nicolas Monardes' work: "Joyfull newes out of the newe founde worlde," English translation by FRAMPTON, merchant anno 1577. Introduction by GASELEE, Knopf, New York City, **1925,** Vol. I, p. 92.

[3] The Academy of Science at Paris devoted thirty years of work to the analysis of plants by this method—JAGNAUX, "Histoire de la chimie," Baudry et Cie., Paris, **1891,** Vol. 2, p. 453. For an interesting article on this subject see NIERENSTEIN, "A missing chapter in the history of organic chemistry: the link between elementary analysis by dry-distillation and combustion," *Isis*, **21,** 123–30 (1934).

[4] STILLMAN, "Chemistry in medicine in the fifteenth century," *The Scientific Monthly*, **6,** 167–75 (1918).

[5] STILLMAN, *loc. cit.*

It is in one of the works of a disciple of Paracelsus that we find the first reference to an "oil" from tobacco. Jacques Gohory, editor of the first French edition of the works of Paracelsus,[6] has received but little attention in

From Le Févre's "Traité de la Chymie," Paris, 1660

APPARATUS FOR DISTILLING WATERS, SPIRITS, AND OILS WITH A VESSEL FOR SEPARATING THE DISTILLED OILS

the histories of chemistry.[7] He was born in Paris in January of the year 1520,[8] a member of the legal aristocracy by birth. The greater part of his career was spent at court and on diplomatic missions abroad, yet he found time to write, translate, and edit many works, among which only a few are of scientific interest.[9] It was in 1556, upon returning from a mission to Rome, that he decided to retire from the court and devote himself to the quiet study for which his talents were best adapted. The works of Paracelsus, who had died only fifteen years before, influenced him greatly, and he gave himself over to alchemical experiments. It seems that he spent many of the years of his retirement (1556 to 1570 or 1571) practically in solitude, studying the works of the great chemist whom he characterized as "the most earnest of the doctors and the most subtile philosopher of his time."

It is quite natural that a man so well schooled in the works of Paracelsus and who "followed the new discoveries in America with great interest, seeking to learn about the new plants which had been brought back to Europe"[10] should investigate tobacco in a manner which would bring a crude form of nicotine to light. In 1572 Gohory founded a botanical garden in Paris (Saint-Marceau-les-Paris) which was a precursor of the Jardin des Plantes founded sixty years later. Here in a small laboratory he tried many experiments, some undoubtedly for alchemical purposes, others with more practical ends.[11] And so we find in Gohory's "Instruction sur l'herbe petum," published in Paris in 1572 (and incidentally the first French work devoted principally to tobacco) the following passage:

> "La feuille simple sert de remede en sa verdeur. Il s'en tire eau par distillation d'alembic. Il s'en tire huille par desensoire de verre en cornue de verre.[12] Il s'en fait sel."

The "oil of tobacco" was used principally as an external remedy for skin diseases. Doubtless its offensiveness had much to do with the general belief in its efficacy. On throughout the seventeenth and eighteenth centuries we find mention in chemistries and pharmacopoeias of the oil of tobacco—always obtained by some form of distillation of the crude leaves.[13]

Among the most elaborate and complete descriptions we have found is that in the "Traité de la chymie" of Nicolas Le Févre, published in Paris in 1660. Perhaps a few remarks about Le Févre would not be amiss here, for although he has been called representative of the best chemists of his time[14] he has been somewhat neglected by historians of chemistry. Nicolas Le Févre lived during a vital period in the history of science. A graduate of a Protestant academy in Sedan, he was chosen demonstrator of chemistry at the Jardin des Plantes by Vallot, physician to the king. Here, according to Hoefer,[15] he may well have shone, his known proficiency as a manipulator contrasting sharply with the vaporous theoretical considerations of the professor. It is said[16] that he was allowed to give courses himself and that these were very successful, being attended by Kenelm Digby and John Evelyn, later to be charter members of the Royal Society, as well as by the exiled Charles II. That the latter was impressed by Le Févre we shall presently see.

In 1660 two events occurred in his career. First, the book, "Traité de la Chimie," his chief contribution to chemistry, appeared.[17] Second, in November he received an invitation from the newly reinstated Charles II of England to take charge of the laboratory

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[6] "Theophrasti Paracelsi Philosophiae et Medecinae utriusque Compenium, ex optimis quibusque eius libris: Cum scholiis in libros IIII eiusdem *De Vita Longa*, plenos mysteriorum, parabolarum, aenigmatum, Auctore Leone Suavio I.G.P. Vita Paracelsi, Catalogus operum et librorum. Cum indice rerum in hoc opere singularium," Paris, **1568**.

[7] See HOEFER, "Histoire de la chimie," Didot Frères, Paris, **1843**, Vol. 2, p. 108, for the only such reference we have found.

[8] BOWEN, Harvard Thesis, Sept., 1935, p. 2.

[9] Besides the works of Bowen aforementioned, see HAMY, *Nouvelles Archives*, Paris Museum d'histoire naturelle, (4) **1**, 1–26 (1899).

[10] BOWEN, Thesis, p. 71.

[11] HAMY, *loc. cit.*, p. 17.

[12] Folio 7, v°–8°. Probably this is the same sort of distillation process which Boerhaave describes under "Distilled oils per descensum"—see his "Elements of chemistry," translated by DALLOWE, London, **1735**, Vol. 2, p. 85.

[13] See SCHRODER, "The compleat chymical dispensatory," translated by ROWLAND, London, **1669**, p. 434; LEMERY, "A course of chymistry," translated by HARRIS, London, **1677**, p. 288; and many others.

[14] DUMAS, "Leçons de philosophie chimique," Bechet jeune, Paris, **1837**, p. 51 *et seq.*

[15] HOEFER, "Histoire de la chimie," 2nd ed., Didot Frères, Paris, **1869**, Vol. 2, pp. 276–81.

[16] DE ROSEMONT, "Histoire de la pharmacie à travers les âges," Peyronnet et Cie., Paris, **1931**, Vol. 2, pp. 28–9.

[17] His only other contribution is that he is said to have discovered mercuric acetate and brought it to the attention of physicians.

at the Palace of St. James as Royal Professor of Chemistry.[18] Undoubtedly the appointment was a welcome one, since England was relatively poorer in chemists (excepting the great Boyle, of course) and offered a much pleasanter situation for one who, like Le Févre, belonged to the "religion réformée." Here at the court of Charles II experimentation was popular and there was a great deal of dilettante interest in science—an interest which had at least one good outcome in the incorporation of the Royal Society.[19]

As evidence of the importance of distillation in the minds of practical chemists of that time it may be noted that Le Févre's title as given in the 1662 edition of his book[20] was "Apothecary in Ordinary and Chymical Distiller to the King of France, and at present to his Majesty of Great Britain."

Whether Le Févre found England to his liking is not stated. That he was soon recognized professionally is evidenced by his appointment as a member of the Royal Society on May 20, 1663, but that he had difficulty in drawing his salary from the never-opulent court of Charles II is suggested by the aforementioned petition in the "Calendars of State Papers." He died in London in 1669.

Le Févre's ideas were not advanced for the time but were rather representative of the period. As one much concerned with the process of destructive distillation it is not surprising that he subscribed to five elements, corresponding to the fractions which Paracelsus mentioned in the passage which we have already quoted.

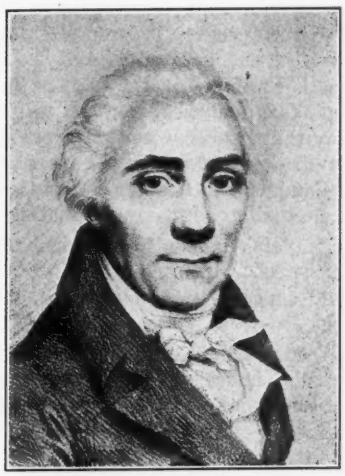
Returning to Le Févre's book we find a detailed description of the distillation of tobacco, given as an illustration of the separation of the elements as well as for its medicinal importance. Le Févre's process was essentially the steam distillation by which one would obtain nicotine today. As the water was driven off from the leaves it carried with it the nicotine and in the receiver we find a layer of water and one of the crude "oil." These were separated in a special vessel and the oil used:

"exterieurement . . . pour consolider les playes récentes, pour mondifier & pour guerir tous les mauvais ulceres & pour oster les accidens des contusions, parce qu'elle resout puissamment le sang extravasé, & qu'ainsi elle empesche la chaleur l'inflammation qui precedent tousiours la suppuration."

After purification the oil was suitable for use internally against suffocation, "strangulation of the womb," inflammation of the spleen (short breath), as well as a good anti-epileptic "when given during the decline of the moon in theriacal spirit of camphor." He concludes by saying:

"Peut-estre que beaucoup de personnes s'etonneront de ce que i'attribue tant de si belles & de si differentes vertus aux remedes qu'on tire du tabac: mais ie sçay que leur estonnement cessera, lors qu'ils prendront la peine de faire reflexion sur les differens usages, ausquels le commun peuple, les Chirurgiens & les Medcins mesmes appliquent la plante recente, ou ses feüilles apprestees & sechées."

So much for the early empirical work on nicotine.



LOUIS NICOLAS VAUQUELIN, CHEMIST AND ANALYST; THE DISCOVERER OF CHROMIUM

We have to wait until the year 1809 before finding any chemical investigation of tobacco in the modern sense. Then, among the multitudinous papers of that all-searching analytical chemist, Louis Nicolas Vauquelin, we find one in the *Annales de chimie et de physique*[21] where is described a thorough, painstaking analysis of Virginian tobacco. We might well expect such a paper at this time, since the first two decades of the nineteenth century, although relatively unproductive of fundamental theoretical advances, formed a period of intense and widespread investigation of natural products. Vauquelin (together with the German, Martin Heinrich Klaproth) may be described as the dean of the analysts of this period. The mere list of his papers in the Catalogue of the Royal Society occupies fourteen pages and we owe to him such diverse contributions as the discovery of the element chromium[22] and the isolation of quinic acid. His publication on tobacco in 1809 was the result of a long and arduous investigation in which he was aided by two other interesting characters. One was Pierre-Jean Robiquet whom Vauquelin describes in this paper as a "jeune pharma-

[18] Most sources (Hoefer, Kopp, Dumas) state that Le Févre transferred to England in 1664. This appears to be erroneous since a note written by L. J. H. Bradley (*The Times Literary Supplement*, July 22, 1926, p. 496) states that Le Févre's appointment is recorded in a warrant dated November 15, 1660. In the "Calendars of State Papers" for March 14, 1663, is found a petition by Le Févre for arrears of pay from September 30, 1660.

[19] Evelyn says of the king, "He knew of many empirical medicines and the easier mechanical mathematics." ("The dictionary of national biography," Humphrey Milford, London, 1917—Article on Charles II.) In the same place we find, "His liking for chemistry, which he shared with his cousin, Prince Rupert, was long-lived; in the very month of his death he was engaged in the production of mercury."

[20] See BRADLEY, *loc. cit.* Apparently this is an English translation of the 1660 edition.

[21] Vol. 71, 139–57 (1809).

[22] WEEKS, "The discovery of the elements," 3rd ed., JOURNAL OF CHEMICAL EDUCATION, Easton, Pa., 1935, pp. 58–63.

cien de Paris" and in another place "jeune chimiste, qui réunit à la solidité du raisonnement une grande habilité dans les expériences."[23]

Robiquet is to be remembered as the discoverer of the alkaloids narcotine (1817) and codeine (1832). The other collaborator of Vauquelin's was an American, David Baillie Warden,[24] who was at that time Consul *pro tempore* at Paris. Although Warden's name seems to appear nowhere else in the chemical literature and he was only a chemist by avocation it is of interest to note him here as an example of the many early Americans who were interested in science.

To return to Vauquelin's paper: Using what is essentially the modern procedure he prepared a fairly pure sample of nicotine and isolated as well the malic acid with which it is combined in the plant. But, despite all Vauquelin's fine analytical work on this substance, we cannot say that he discovered nicotine, for the discovery of an alkaloid rests upon the recognition of its basicity and Vauquelin, although he noted the alkalinity of his product, attributed it to contaminating ammonia.

Before we leave Vauquelin let us recall the familiar story of a little event which happened in the fall of the year 1808 and concerns two of the characters in our story.[25]

War had been declared with Spain and it became necessary for all Spaniards in Paris to register with the authorities. One young Spaniard—a student of Vauquelin's—applied, together with a fellow countryman of his, at the prefecture of police in order to obtain a civilian pass. After long hours of questioning the two were imprisoned and spent the night drearily in the jail. In the morning the young student was called into the office where, instead of the endless questions which he expected, he found his master, Vauquelin, dressed in the formal attire of the Institut with all his regalia and a sword at his side. "Je viens réclamer monsieur," said Vauquelin to the officer in charge. "Je résponds de lui; il ne troublera jamais l'Etat. Je l'emmène." And the young Spanish student was free—Matthieu Joseph Bonaventure Orfila, eminent chemist and the founder of modern toxicology, whose name appears later in the history of nicotine.

The first forty years of the century witnessed the discovery of many alkaloids.[26] In the midst of this period nicotine was really discovered. It was in the year 1828 that an annual prize was offered at the University of Heidelberg for the best paper on the active principle of tobacco and upon its physiological action. The prize was won by Christian Wilhelm Posselt and Karl Ludwig Reimann for a paper[27] which they presented with the motto: *In magnis voluisse sat est.* These two were young students: Posselt,[28] who did the physiological part of the work, later became a physician in Heidelberg and eventually professor extraordinary in the medical faculty of the University; Reimann,[29] who had been an assistant of Geiger's at Jena, became a manufacturing chemist and is said to be the inventor of an industrial process for making racemic acid as well as the first to manufacture tartaric and acetic acids on a plant scale.

The prize-winning paper appeared to settle the question of the character of nicotine and yet it was met in many quarters with disbelief. Chemists of the time were loath to believe that a pure alkaloid could be liquid. So great was the scepticism and controversy over the matter that a society of apothecaries in Paris appointed a committee to reinvestigate the whole question. The resulting report of Henry and Boutron-Charlard[30] fully supported Posselt and Reimann, and nicotine was finally accepted as an alkaloid.

Besides these men whom we have mentioned there were many others during the first half of the century who worked with nicotine. Almost all of them stressed the great poisonousness of the alkaloid—rightly so perhaps because it is among the most virulent poisons known. The information seems to have become common knowledge and lead to at least one unfortunate abuse of the compound.

The once sensational *affaire Bocarmé*, which, if we are to believe the accounts of the time, made a great furor in Europe, entails a grim story whose details are best left buried in the annals of medico-legal literature.[31] But the scientific aspects of this celebrated murder case have some interest in the history of chemistry. For one thing, they involve a little appreciated side of the great Belgian chemist, Jean Servais Stas, a man who is rightly remembered for his truly magnificent determinations of atomic weights. Stas felt that he had a public duty as a chemist and he was frequently called upon to aid various authorities in chemical matters.[32] Thrice he had investigated suspicious materials and

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[23] DAINS, "Pierre-Jean Robiquet 1780–1840," The New York Quinine and Chemical Works, Brooklyn, N. Y.

[24] David Baillie Warden, diplomat, author and book collector, was born in 1772 in Ireland. He attended the University of Glasgow and was licensed to preach in 1797 by the Presbytery of Bangor. In 1799 he was forced to emigrate to the United States because of his political activities. In 1804 he became a citizen and went to Paris as the private secretary of General Armstrong, minister to France. He spent the rest of his life in Paris, holding the Consulship there from 1808 to 1810. He made two large collections of books relating to America, one of which is now in the Library of Harvard University and the other in the New York State Library. He wrote several works on the history of America. (MALONE, editor, "Dictionary of American biography," Scribner's, New York City, **1936,** Vol. 19, pp. 443–4.)

[25] FAVOL, "La vie et l'oeuvre d'Orfila," Albin Michel, Paris, **1930,** (told largely in Orfila's own words). WEEKS, "The discovery of the elements," 3rd ed., JOURNAL OF CHEMICAL EDUCATION, Easton, Pa., **1935,** p. 62.

[26] The German, Friedrich Sertürner, isolated the first alkaloid in 1805. By 1835 thirty compounds of this class were known.

[27] Geiger's *Magazine f. Pharm.*, **24,** 138–61 (1828).

[28] POGGENDORFF, "Biographisch-Literarisches Handwörterbuch zur Geschichte der exakten Wissenschaften," Leipzig, **1863,** Vol. 2, col. 508.

[29] POGGENDORFF, *op. cit.*, Leipzig, **1863,** Vol. 2, col. 595; **1898,** Vol. 3, col. 1101.

[30] Erdmann's *J. prakt. Chem.*, **10,** 209–22 (1837).

[31] STAS, "Oeuvres complètes," C. Muquart, Brussels, **1894,** Vol. 2, pp. 175–303. Recherches médico-légales sur la nicotine. (From *Bull. Acad. royale de méd. de Belg.*, **11,** 202 (1851–52.))

[32] TIMMERMANS, "Jean Servais Stas," J. CHEM. EDUC., **15,** 353–7 (1938).

found alkaloids present, and when in November, 1850, the Count and Countess Bocarmé were accused of poisoning the countess's brother in their castle at Bury in the Department of Hainaut, Belgium, Stas was called

JEAN SERVAIS STAS IN 1851. FRONTISPIECE TO VOLUME 2 OF HIS COLLECTED WORKS

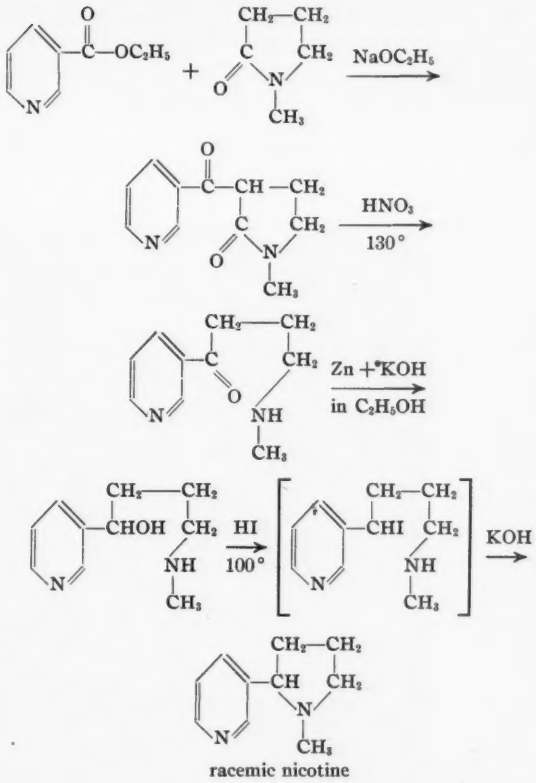
in to investigate. Nicotine was the suspected agent and in a typically painstaking research Stas proved this to be the case. The method of detecting alkaloids which Stas worked out on this occasion, later slightly modified by Otto, is now the standard method employed in the toxicology of the alkaloids.

Another great chemist was unofficially involved in this case of nicotine poisoning. Orfila, of the Faculty of Medicine of Paris, heard of the case and, after going to Belgium to obtain some details, he carried out a number of toxicological experiments on animals, finally arriving at a process similar to that which Stas had evolved. Unfortunately this was published[33] after Stas had completed his work but preceding the trial, when, of course, Stas's lips were officially sealed. The Belgian press loudly accused Orfila of cheating Stas of his credit and naturally the latter was much displeased by the unfortunate publication but, when he was finally able to present his research he gave due credit to Orfila, yet proved that he himself was the originator of the method. For once, fate gave credit to the right man and today we remember his method as the "Stas procedure."

The rest of the incidents in the history of nicotine are typical of the steps through which we must pass in understanding the structure of natural products. Melsens (incidentally a close friend of Stas's) in 1843, using the then new organic analytical methods, arrived at the correct formula for nicotine,[34] Barral and Ortigosa having just previously obtained nearly the same results.

The elucidation of the structure and the final synthesis of nicotine are triumphs of modern organic chemistry. It would be quite fruitless here to trace each fact which led up to the correct conclusion as to the structure. Suffice to say that in the eighties and early nineties the nature of nicotine was the subject of many conjectures and discussions. With A. Pinner's work[35] in 1893 the now accepted structure of nicotine was put forward and awaited only the absolute proof of synthesis—proof soon to come in the form of a series of papers by the Swiss, Amé Pictet.[36] These truly beautiful researches of Pictet's, wherein he synthesized nicotyrin, dihydronicotyrin, the oxidation products of nicotine, and finally nicotine itself, constitute a well-known monument in alkaloid chemistry. The brilliance of the final successful synthesis in 1904 of optically active nicotine, identical with the natural product, is only dimmed by the other gems of synthesis which

SPÄTH AND BRETSCHNEIDER'S SYNTHESIS



racemic nicotine

[33] ORFILA, "Mémoire sur la nicotine," *Annales d'hygiene publique et de médecine légale*, **46**, 147–230 (1851).

[34] *Ann. de chim.*, (3) **9**, 465–72 (1843).

[35] *Ber.*, **26**, 292–305 (1893); *Archiv d. Pharm.*, **231**, 378–448 (1893).

[36] PICTET AND ROTSCHY, *Ber.*, **37**, 1225–35 (1904). For biographies, see CHERBULIEZ, *Helv. chim. Acta*, **20**, 828–45 (1937), and COX, *J. Am. Chem. Soc.*, **60**, 1 (1938).

Pictet later presented to the world. Unfortunately some steps of the synthesis required such violent conditions as to throw doubts on the value of the whole as a proof of structure. A later synthesis by Späth and Bretschneider[37] in 1928 was carried out under much milder conditions but serves only to confirm Pictet's results.

AMÉ PICTET

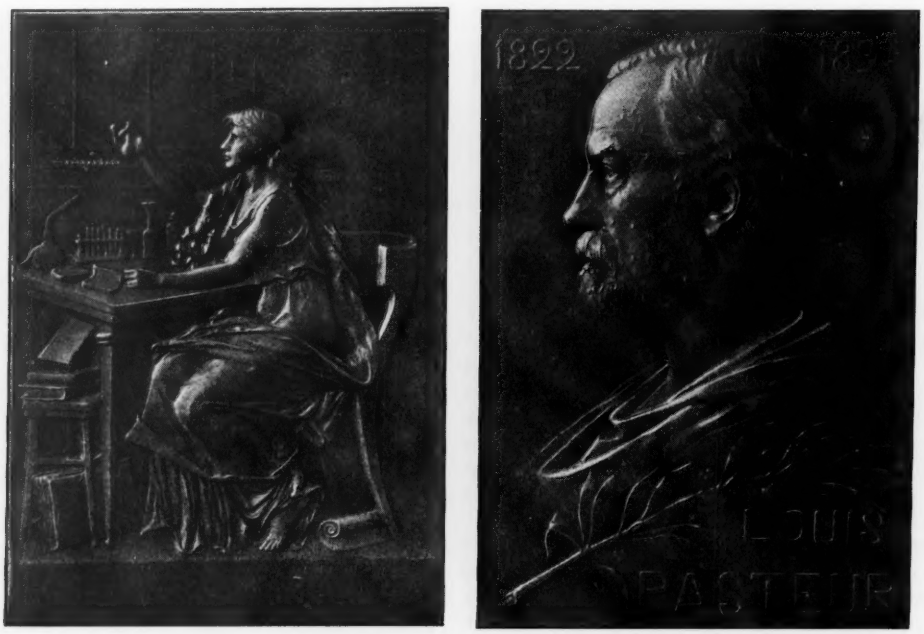
The history of nicotine is by no means closed. Today, tons of it are being used in the form of a strong aqueous infusion of tobacco waste for ridding plants of parasites. Nicotine sulfate, more stable, less volatile and poisonous than the free base, is also much used for this purpose and finds application as well in the treatment of internal parasites in poultry.[38]

Of great importance is the recent discovery that nicotinic acid is the (or at least one of the) pellagra-preventive factors in the vitamin B complex. Nicotinic acid was first discovered by Carl Huber in 1867[39] who obtained an "Amidosäure" from nicotine by chromic acid oxidation. A few years later he recognized the true character of his derivative as a pyridine carboxylic acid.[40] Nicotine is at present the commercial source of pharmaceutical nicotinic acid. During the recent Spanish Civil War twenty-five pounds of nicotinic acid were shipped in one lot to Spain from the United States to alleviate the pellagra resulting from malnutrition. Thus in one small way the extravagant hopes of the early pharmacists for nicotine as a medicine have now been realized.

The writer wishes to express his sincere thanks to Dr. Willis H. Bowen of the University of Nebraska for kind permission to include material from his Harvard Thesis on Jacques Gohory.

[37] *Ber.*, **61**, 327–34 (1928); CRAIG [*J. Am. Chem. Soc.*, **55**, 2854–7 (1933)] has offered a third synthesis of nicotine.

[38] DEONG, *J. Ind. Eng. Chem.*, **16**, 1275–7 (1924).
[39] *Ann.*, **141**, 271 (1867).
[40] *Ber.*, **3**, 849 (1870).



(From the Lyman C. Newell Collection)

OBVERSE AND REVERSE OF THE BRONZE PASTEUR COMMEMORATIVE PLAQUETTE, STRUCK BY THE FRENCH MINT

The Function of General Chemistry[1]

HUBERT N. ALYEA *Princeton University, Princeton, New Jersey*

WE ARE chemists by profession because we are experimentalists by nature, and because some years ago when we were students, our chemistry teachers wisely encouraged us in experimental research, and we liked it.

It is *our* duty, in turn, to imbue the next generation of young men with the understanding and spirit of research; and that, I believe, is the prime function of the general chemistry course.

Let me be more specific about research. Some years ago I was curious about the reaction between hydrogen and oxygen. These two gases explode under certain conditions only at low pressures. Why? Why does increasing pressure, which *increases* the number of molecules, *decrease* rate of reaction? How do the hydrogen and oxygen molecules interact? Why does packing the vessel with glass wool prevent explosion? Why does washing the vessel with a solution of potassium chloride retard the reaction? A thousand and one questions flooded my mind, clamoring for answer. I had experienced the first stage in the life history of research: *curiosity.*

There was but one way to find answers: to learn everything about hydrogen and oxygen. Into the chemistry library I went. I read hundreds of articles. I took copious notes. I became a storehouse of knowledge on the hydrogen-oxygen reaction. I became an authority. I had traversed the second stage of a research: *fact-finding and the acquisition of knowledge.*

Finally I entered the last phase. I uncovered conflicting statements among the authorities. I discovered that often they knew less, but wrote more, than I. I took issue with their conclusions. I challenged their theories, and devised and carried out experiments testing whether their theories or mine were correct. In the end I experienced the glowing reward which comes from original research: I made discoveries.

Now you all, as research chemists, have passed through these same three stages, culminating in the joy of discovery. And I maintain that the function of general chemistry is to give this same experience to the student.

First, to arouse his *curiosity.* It is our heritage. Our predecessors, the alchemists, certainly wondered.

> "Superstitious, often dishonest, . . . without this blind groper after the hidden mysteries of energy and matter, modern chemistry would never have been born. I can see him now, working over his pots and retorts in crude laboratories and dark caves . . . his imagination often fired with lofty zeal, exercising an almost infinite patience as with the passionate purpose of a religious fanatic he sought to find or make the Philosopher's Stone."[2]

Now the march of time takes us forward three hundred years into a little apothecary shop in Göteborg, Sweden, at the time of the American Revolution. The keeper of the shop is an ardent experimentalist, Carl Wilhelm Scheele, discoverer of chlorine, tungsten, molybdenum, oxygen. Eking out a meager existence, struggling against ill health which struck him down at the early age of forty-four amidst a life of feverish activity, he writes:

> "Oh how happy I am. No care for eating or drinking or dwelling, no care for my pharmaceutical business, for that is mere play to me. But to watch new phenomena—this is all my desire, and how glad is the enquirer when discovery rewards his diligence; then his heart rejoices."[3]

This love for fathoming the mysteries of natural phenomena was well phrased by Wilson, biographer of Sir Henry Cavendish, when he wrote:

> "His Theory of the Universe seems to have been that it consisted *solely* of a multitude of objects which could be weighed, numbered, and measured; and the vocation to which he considered himself called was to weigh, number, and measure as many of those objects as his allotted three score years and ten would permit."[4]

It is difficult for us, as scientists, to realize that our students may not necessarily be enthusiastic about natural phenomena; and that our first task is to stimulate their curiosity. Their natural sphere of appreciation may lie in the beauty of words, or in the harmony of music, or in the loveliness of a piece of sculpture, architecture, or a painting. It is for us to divert their appreciation to the beauty of truth. For truth is the god of our profession. Let us read what an artist says about us.

> "The scientists regard *truth* as the paramount issue . . . they crave a meticulous precision of observation, measurement, and statement quite alien to the other teachers of men. They exhibit an almost shocking insensibility to the cherished motives of belief. They do not ask whether what is sought is right or wrong, beautiful or ugly, useful or futile, comforting or distressing. They only ask whether what is found is an instance of something really happening."

And so our primary duty, as teachers, is to arouse the curiosity of the student in natural phenomena.

Next he must learn facts. Mendeleeff writes:

> "Refrain from illusions, insist on work and not on words. Patiently search divine and scientific truths."[5]

We must impress upon the student that he is working in the *labor*atory, which means he must labor; that the important discoveries of science are not plucked from

[1] Contribution to a Symposium on the First Two Years of College Chemistry conducted by the Division of Chemical Education at the 100th meeting of the A. C. S., Detroit, Michigan, September 9–13, 1940.

[2] DARROW, "The story of chemistry," Bobbs-Merrill Company, Indianapolis, Indiana, **1930**, p. 2.

[3] SCHEELE, Letter to Gahn, 1775.

[4] WILSON, "Life and works of Cavendish," Harrison and Son, London, **1851**, p. 186.

[5] MENDELEEF, "Solutions," Demarkova, St. Petersburg, **1887**, Preface. (In Russian.)

the tree of knowledge like bunches of grapes, but painstakingly and laboriously dug up like potatoes or peanuts.

Third, we must teach the student *critical judgment.* This includes a number of factors. It includes sensible and extensive application of the many principles taught him, interpretation of graphs, and correlation of data in tables and graphs. It includes, also, encouraging the student to disagree with the teacher, with the textbook, and with the laboratory manual in the light of his own observations. Hildebrand[6] relates that his most satisfying research was carried out as a high-school student, wherein he disproved the statement of an eminent Harvard chemistry professor. That, I submit, is an excellent recommendation for the high-school teacher, who could so fortify his pupil in the exercising of critical judgment that he dared to disagree with a Harvard professor.

The student must be taught the suspended judgment of the scientist, who decides temporarily, and will change if shown something better to change to. The student must understand that much he learns today may be different tomorrow, and different because of discoveries which he himself may make. Atomic structure, the concept of acids and bases, the theory of ionization: all will be altered for convenience. He must realize the suspended judgment of the scientist who says:

"Say not this is the truth, but so it seems to me to be as I now see the thing I think I see."

The student who experiences the delight of exercising this critical judgment will need no coaxing to add to his fund of knowledge. He will realize readily that a firm foundation presages sound judgment. As Kekulé related in his discovery of the ring structure of benzene as he sat dreaming before his fireplace:

"But look! What was that? One of the snakes had seized hold of its own tail, and the form whirled mockingly before my eyes. As if by a flash of lightning, I awoke; and this time also I spend the rest of the night in working out the consequences of the hypothesis. Let us learn to dream, gentlemen, then perhaps we shall find the truth . . . but let us beware of publishing our dreams before they have been put to the proof by the waking understanding."[7]

The function, then, of general chemistry is:

(1) to arouse curiosity
(2) to implant knowledge
(3) to cultivate judgment.

The relative emphasis on these three items depends naturally upon the particular course and its relation to the subsequent program of the student. By electing the advanced general chemistry course, the student has already indicated his scientific bent and his stimulated curiosity, so that a fundamental training in advanced inorganic chemistry and the exercising of sound judgment is prescribed. On the other hand, for the beginner who will probably not continue in chemistry, curiosity and judgment are paramount; while knowledge is merely of transient importance. In either event we seek to duplicate for the students the experiences we ourselves have had in our own research. Then it is that the students realize why we are fascinated by chemistry, why we cling to our profession, why we enjoy the laboratory despite the smells and smokes, filth and fumes, dirt and poverty; and, like the alchemist of old, with curiosity impelling us, with knowledge sustaining us, with criticism and discovery thrilling us,

"among all these evils (we) seem to live so sweetly that (we should) die if we (should) change places with the Persian King."[8]

[6] HILDEBRAND, J. CHEM. EDUC., **17**, 414 (1940).

[7] JAPP, "Kekulé Memorial Lecture," *J. Chem. Soc.* (London), **73**, 100 (1898).

[8] BECHER, "Acta laboratorii chymica monacensis, seu physica subterranea," **1669**, Preface.

EVOLUTION OF THE EQUILIBRIUM SYMBOL AS USED IN CHEMISTRY

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Bureau of Entomology and Plant Quarantine, Beltsville Research Center, Maryland

THE conventional equation sign (=) in chemical equations has within the last thirty years been replaced to a large extent by two arrows (⇄) showing reversibility of a reaction. Both the length (⇀↽) and the thickness (⇄) of the shafts of the arrows have been used to designate the direction in which the reaction tends to go to completion. The top arrow signifies the original direction of the reaction.

Usage of the two arrows, modified so that they may lie closer together, has resulted in the removal of the lower barb of the upper arrow and the upper barb of the lower arrow. This symbol (⇌) has found wide usage in modern chemical literature.

In line with this development, we offer the suggestion that only one double-barbed horizontal line or shaft be used to denote a reversible reaction. This is accomplished by superimposing the shafts of the "half arrows" (↼⇁). The upper barb would indicate the original direction of the reaction and the length of the barb (↼⇁) or its thickness (↼⇁) would show the dominant tendency. It appears that the use of this simplified symbol should facilitate the writing of chemical equations.

[1] Present address: National Bureau of Standards, Washington, D. C.

Making Fused Porcelain-Pyrex Filters

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A NOTE appeared in the June, 1940, number of the *Analytical Edition* of *Industrial and Engineering Chemistry* by C. A. Roswell (*1*) describing the sealing of a porcelain plate into a pyrex body tube to make a small Büchner funnel. Roswell referred to Frary *et al.* (*2*) in regard to the sealing of pyrex to porcelain. Neither Roswell nor Frary mention fusing *unglazed* porcelain filters into pyrex. The writer has been told that for some time one of the supply companies sold a filter which consisted of a porous porcelain plate fused into a pyrex funnel, but that this article was discontinued.

Unglazed porcelain, specially made for filters,[1] has properties which make it highly satisfactory as a material for the amateur glass blower, and as a means of accomplishing certain operations, notably the very fine dispersion of gases in liquids, and the removal of small amounts of very fine precipitates, or of traces of water from liquids, such as extracts in ether. Its use as a filtering medium may have been unpopular because it is too fine for many purposes. However, when a liquid fails to flow through at the pressure of its own head in the funnel, it may be found to flow rather freely when a small additional pressure or suction is applied.

The porcelain itself is easily cut and shaped. With a little patience special shapes can be cut with a sharpened file. It is ground so fast on a glass-cutting stone[2] that care must be taken to avoid exerting too much pressure against the stone and cutting away porcelain beyond the desired depth. The shaping of the piece can be finished with an ordinary triangular file of the kind usually used to cut glass tubing. Iron from the file can be removed, and the edge can be worked to a uniform velvety finish to make a tight joint with the pyrex, by rubbing it with another piece of the same porcelain.

It is, if anything, easier to fuse pyrex to porcelain than to a similar piece of glass, especially to sintered glass, because the porcelain does not collapse at the temperature of fusion. Sintered discs show a band of fused glass at the edge in which the pores are changed or obliterated, but no such change is visible in porcelain, and the filtering area is undiminished. The porcelain will not crack unless the heating is excessive or prolonged. Chipping of the edge occurs only if heating is more rapid than it would be in making an ordinary ring seal with glass. The pyrex is hotter than in a glass-to-glass fusion, hence the glass flows well and makes a good joint. When a good job has been done, the surface of the porcelain, viewed through the glass, has the same appearance as the surface of a piece before contact with glass; it is free of bubbles or cloudiness. At the high temperature used, pyrex adheres to porcelain so that a bead or ring of glass can be built up using 2-mm. glass rod, to prepare the piece for attachment to a support or for fusion onto a glass tube, or for other purposes.

Recently, three types of filter have been prepared having pyrex-to-porcelain joints, and have given satisfactory performance over a period of months. Two common forms of filtering funnel are shown in Figure 1. These need no explanation.

FIGURE 1.—SIMPLE FILTER FUNNELS WITH POROUS PORCELAIN DISCS

In Figure 2 is shown a candle-type filter, two of which were used in the bottom of a column for the absorption of a gas in a liquid. A shallow groove was cut in the porcelain about 5 mm. from the open end, using a file and then rounding and smoothing the groove with a piece of porcelain. Using a slender pyrex glass rod, a ring was formed around the piece in the groove. This was heated until the glass flowed out smoothly, filling the groove and showing a sharp neat junction with the unglazed porcelain at its edge. The glass partition to be used in forming the ring seal was then built up by fusing on glass rod while the piece was slowly and uniformly rotated. The ring of glass so formed was fused into the tube forming the bottom of the column. The joints thus formed are likely to crack because of their great rigidity unless they are immediately placed in a

[1] "Selas," porosity 10 was usually used.

[2] Norton, No. 37150–1.

hot annealing oven (550°–570°C.), but they do not seem to be more fragile than a similar rigid all-glass joint, and after being well annealed the ones tested have proved to be strong.

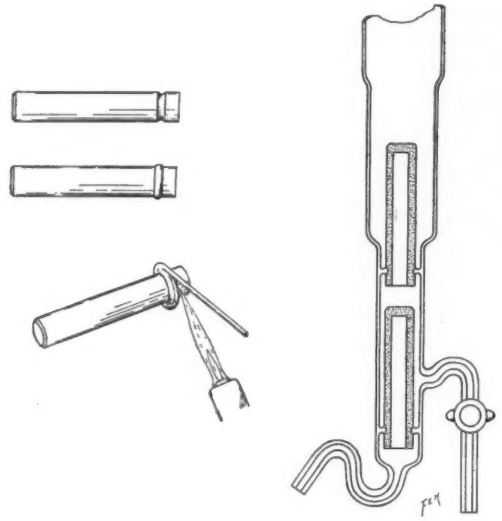

FIGURE 2.—CANDLE-TYPE FILTERS. METHOD OF BUILDING UP GLASS RING (LEFT) AND SECTION OF FILTERS IN PLACE IN A COLUMN (RIGHT)

The column has been used to prepare calcium-free sodium bicarbonate for intravenous use from saturated sodium hydroxide by diluting and saturating with carbon dioxide. The lower filter prevents dirt from the rubber tubing from getting into the apparatus with the carbon dioxide, and also distributes the gas in the chamber between the filters, keeping the liquid saturated while it is being drawn off. The upper filter distributes the gas in the liquid as a cloud of fine bubbles when the outlet is closed, and then acts as a filter when this stopcock is opened to allow liquid to flow out.

The filter shown in Figure 3 is presented chiefly as an illustration of the technic of fusing a tube to the flat face of a porcelain disc. It was satisfactory as a filter and as a means of conducting upward-flowing solvent into a sample that was being extracted, but, at the pressure available, it was too fine to permit the passage of solvent vapor as originally intended.

To accommodate the edge of the inner glass tube, *E*, a circular groove was cut in the face of the porcelain plate to a depth of about half the thickness of the plate by rotating the tube itself against the plate by hand, exerting only light pressure and guiding the cutting edge by means of a thin board having a hole through which the glass tube fit freely, *A*. Very finely ground pyrex powder was used to fill the narrow space between the walls of the groove and the tube. The porcelain plate with the glass tube in place on top was then placed on the floor of the furnace. The door of the furnace was left slightly ajar to prevent overheating the glass above the joint, and the electric heating elements were turned up until the floor of the furnace and the porcelain disc were bright red. Fusion of the joint was judged by shrinkage of the powdered glass. The temperature of the furnace was allowed to drop to 600°C. with the door open, and then cooling was continued with the door closed to anneal the piece.

Since the sintered pyrex powder is itself porous and its pores may be larger than those of the surrounding porcelain, a method of making the glass-to-porcelain joint similar to that used for the candle-type filters is better when slight leakage between the spaces below the annular and the center parts of the filter would be detrimental. A smooth, well-rounded, circular groove is formed in the face of the porcelain plate and is filled with fused glass, *C*. The glass tube is then fused to this circular glass boss on the plate, *D*. It is well to use a piece of porcelain plate larger than that desired for the filter to facilitate handling and to prevent marring or chipping of the filter. After annealing, this excess is cut or ground off.

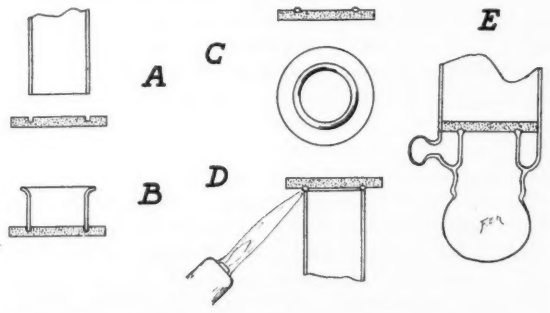

FIGURE 3.—CONSTRUCTION OF ANNULAR DOUBLE FILTER

A. Groove in plate, ground by end of glass tube
B. Finished plate with inner tube attached, cut off, and end rolled. This also shows position in which sintering is done
C. Alternative construction; groove cut and rounded and ring of glass fused to porcelain; section (above) and view of face
D. Fusing of inner tube to circular glass boss
E. Filter plate fused in place in a column, and thin balloons blown out in preparation for attachment of communicating tubes

In describing these filters, the purpose of presenting the filters themselves is secondary to that of calling attention to the variety of pyrex-to-porcelain joints that can be made and of suggesting the technic for the procedure. In a number of chemical methods, the advantage of the elimination of metal or rubber connections is obvious, and whenever the porosity of the porcelain is suitable to the chemical method used, certain advantages cited in the fabrication of porcelain filters will appeal to the glass blower, especially to the amateur.

LITERATURE CITED

(1) ROSWELL, *Ind. Eng. Chem., Anal. Ed.*, **12**, 350 (1940).
(2) FRARY, TAYLOR, AND EDWARDS, "Laboratory glass blowing," 2nd ed., McGraw-Hill Book Co. Inc., New York City, 1928.

An Improved Limestone Analysis for Quantitative Analytical Courses[1]

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PRACTICALLY all modern textbooks of elementary quantitative analysis include directions for a proximate analysis of limestone by gravimetric methods. While this is a good practice exercise, it may be doubted whether it should be considered an inevitable one, at least in its usual form. In an effort to increase the teaching functions of this standard laboratory exercise, and to adapt it for use in warm climates, a modified form of limestone analysis was introduced and tested in the sophomore quantitative analysis courses here several years ago. This analysis was satisfactory enough in use so that it has been continued, with some few minor modifications.

The exercise consists in determining the loss on ignition, silica, and combined oxides by the usual gravimetric methods, calcium by the permanganate method of Kraut (*1*), and magnesium by the method of Stolba (*2*), as modified by Handy (*3*). This series analysis follows a number of the usual partial gravimetric analyses and serves as a transition from the gravimetric to the volumetric part of the analytical work. Since the analysis precedes the presentation of the theory of volumetric analysis, calculations are made on a titer basis rather than by the use of the "normal" system. The required titers are derived from the balanced chemical equations for the simple analytical reactions concerned, by the methods of calculation introduced in freshman chemistry courses. The two volumetric methods may thus be developed without logical difficulties. The standard gravimetric methods for calcium and magnesium are discussed fully in class, using the laboratory work with calcium oxalate and magnesium ammonium phosphate as a background.

The introduction of two standard volumetric methods in the limestone analysis hardly needs any justification, but a few points in favor of the modified exercise may be mentioned. By the time a student has dried and ignited duplicate or triplicate samples of barium sulfate, silver chloride, and hydrous silicon dioxide and ferric oxide, he does not learn much more by drying and igniting a few other precipitates with more or less similar properties. In the modified analysis the time saved by avoiding the slow gravimetric procedures and such futile repetitions is used to obtain an introduction to the titer system, residual titration, and some of the technics of volumetric analysis. It is interesting to note here the comment made by Handy (*3*) regarding Kraut's method: "No one who has adopted the volumetric method for determining calcium oxalate by means of standard permanganate would ever go back to the gravimetric way."

In a study extending over four years with six large classes, it was found that out of 350 students making triplicate limestone analyses by the modified procedure 94 per cent completed all of the magnesium and calcium determinations, while out of 340 students analyzing the same samples in triplicate by the standard gravimetric methods only 72 per cent completed all of these determinations. Somewhat unexpectedly, results of the completed analyses made by the modified method were both more accurate and more precise than those obtained by the gravimetric methods. However, under the conditions of the study, this may be an indirect result of the fact that the gravimetric methods are essentially more time-consuming.

Both volumetric methods work well in the hands of students using them for the first time. Accidents in the volumetric procedures occur no more frequently than in the gravimetric ones. Provision is made for accidents occurring late in the series analysis by allowing rerun analyses of calcium carbonate samples and magnesium sulfate solutions.

The limestones for analysis contain between 23 per cent and 36 per cent of calcium and 2 per cent to 10 per cent of magnesium. For one-gram samples it has been found best to use 0.400$_0$ *N* $KMnO_4$ having a calcium titer of 0.00801$_6$ grams per ml. Porous porcelain crucibles proved unsuitable for use in the calcium determination, due to clogging of the pores by finely divided calcium oxalate. The filter paper technic recommended by Hillebrand and Lundell (*4*) is more economical and satisfactory.

In the magnesium determination 30.00 ml. of 0.400 *N* H_2SO_4 having a magnesium titer of 0.00486 grams per ml. are used, and the excess acid is determined by titration with 0.400 *N* Na_2CO_3, with methyl orange or bromphenol blue as indicator. These reagents give a considerably sharper endpoint than the more dilute acid and sodium hydroxide solutions used by Handy. Sodium carbonate was considered preferable to sodium hydroxide as a stock solution for student use.

LITERATURE CITED

(1) See MELLOR, "A treatise on quantitative inorganic analysis," Charles Griffin and Co., Ltd., London, **1913,** p. 215, or ref. (*4*).
(2) STOLBA, *Chem. Zentr.*, 728 (1866).
(3) HANDY, *J. Am. Chem. Soc.*, **22,** 31 (1900). See also LOW, "Technical methods of ore analysis," 9th ed., John Wiley and Sons, Inc., New York City, **1922,** p. 140.
(4) HILLEBRAND AND LUNDELL, "Applied inorganic analysis," John Wiley and Sons, Inc., New York City, **1929,** p. 501.

[1] Presented before the Division of Chemical Education at the 101st meeting of the A. C. S., St. Louis, Missouri, April 9, 1941.

Equipment for Studying Electrolysis and Conductivity

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EXPERIMENTS to show the differences in the conductivity of solutions are included in practically all laboratory manuals of inorganic chemistry. Usually an apparatus is improvised by using as electrodes two copper wires. The electrodes are connected in series with a lamp, the change in whose brightness serves to show changes in the conductivity of the electrolyte between the electrodes. Ordinarily the lighting circuit is the source of the electric current. The equipment is assembled into a unit which is given out at the stock room or, in some cases, the apparatus is mounted permanently in some corner. As the experiment is usually carried out, small differences in the conductivity of electrolytes cannot be detected by a change in the brightness of the lamp. Furthermore, detectable differences in the brightness of the lamp may be caused by a change in the resistance of the cell due to the change in the distance between the electrodes or in the depth to which they are immersed in the electrolyte. The use of improvised equipment, also, necessitates considerable supervision, since there is danger of a student receiving a severe shock if he is grounded while touching one of the electrodes.

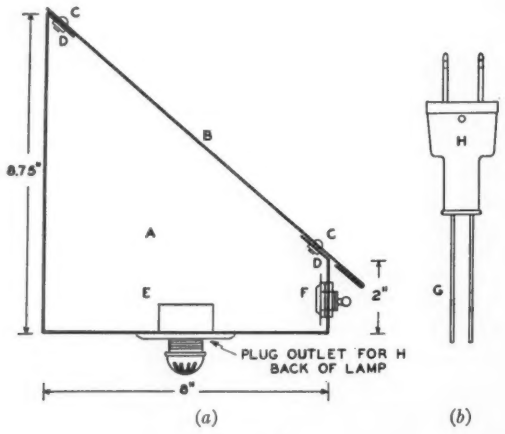

FIGURE 1

To avoid these difficulties the apparatus shown in cross section in Figure 1 was constructed for the use of the large number of students enrolled in the beginning courses in inorganic chemistry. The cabinet *A* and the removable cover *B*, in long sections, were constructed of 16-gage sheet iron. Openings about 2″ × 3″ were made in the bottom of the cabinet at intervals of 18″. A unit *E*, built up of a pilot lamp (Bryant, I.L. 1340) and an outlet (Bryant, I.L. 1320) held in place by a mounting strap (I.L. 1348) was fitted into each hole and the outside was covered with a brown bakelite plate (91021). The lamp was connected to the "live" side of a 110-v. A.C. circuit or the positive side of a source of direct current and to one terminal of the outlet. The other terminal of the outlet was connected to a toggle switch *F*, which was connected to the other side of the 110-v. line. Each unit was connected in parallel with the others. (This unit with appropriate changes in the wiring is used as an outlet for electric irons.) If both A.C. and D.C. are available a double-throw switch appropriately placed makes it possible to use either current. It is desirable though not necessary to place a master switch and fuse on the main line. The metal box was given a crackle finish and grounded.

A work shelf, two inches wider than the cabinet to prevent students from running into the corners, was mounted four feet from the floor and ten inches below the cabinet. The shelf may be hinged so that it may be dropped along the wall when it is not needed.

The electrodes, *G*, made of 16-gage B & S (0.051″) chromel or nichrome wire, were connected to the terminals of a soft-rubber, flat grip cap, *H*, such as is used frequently in making an extension cord. The wires were forced through a rubber stopper (No. 00) cut to an appropriate length. The stopper was then forced into the opening in the cap, holding the wires firmly in place. When the plug is inserted in the outlet in the bakelite plate, the apparatus is ready for use.

The electrodes are about $^1/_4$″ apart and extend $1^3/_4$″ below the handle of the cap. The containers for the solutions whose conductivity is to be determined are 10 × 75-mm. test tubes placed in a test-tube block ($2^1/_4$″ × $8^1/_4$″) holding 16 test tubes. When not in use the cap is attached to the block by slipping the holes in the prongs over a headless nail driven into the wood. By filling the test tubes to the same level and bringing each test tube to the end of the cap, the characteristics of the cell remain constant and the conductivities of different solutions can be compared. Since the filament and the volume of the pilot lamp are small, the change in the intensity of the light with a change in the conductivity of the solution is very pronounced.

The apparatus may be used to carry out the electrolysis of electrolytes by using the socket as a source of direct current. Since a 7-watt lamp is in series with the cell, the maximum current which can pass through the cell is about 70 milliamperes if the voltage is 110. If both alternating and direct current are available, their difference in behavior can be determined.

The apparatus built as described is rugged, attractive in appearance, safe, and easily operated.

Periodical Publications and Agricultural Analysis

A Bibliographical Study

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WHAT we are concerned with here is the selection of periodical sets and current periodicals that should be available to the agricultural research worker in the field of chemistry and to the student of agricultural chemistry. It is definitely true that a large number of research workers and a larger number of students are not aware of the vast amount of periodical literature obtainable in the fields of their particular interest. Consequently not a great deal of this material is employed in their work and studies. With this fact primarily in mind, a tabulation of periodicals used by experts in the field of agricultural chemistry is herein presented.

Two methods of selecting periodicals of the greatest consequence in a certain field are prominent: (1) combining the opinions of a number of specialists in the field, and (2) employing the statistical method on a periodical recognized by leading authorities as basic. One person, even a noted authority in his field, would inevitably exhibit his prejudices and specific needs in compiling a list of journals which he considers indispensable. A selection based on the opinions of a group of specialists must be looked upon with some suspicion too, but perhaps to a lesser degree. It seems reasonable to believe that the most logical means of determining periodical selection is the statistical method, initiated by Professors P. K. L. Gross and E. M. Gross of Pomona College. This criterion eliminates bias and partiality. In considering the desirability of purchasing certain chemical journals, they tabulated the footnote references to other periodicals in a volume of the *Journal of the American Chemical Society*, assuming that this journal was most representative of American chemistry.[1] There has been some criticism of their study, but a more reliable mode of selection has not yet been introduced. "The chief weakness of the procedure is that the final results depend upon the choice of the basic periodical or periodicals. Nevertheless the method has attracted considerable attention."[2] Similar studies have been made for periodicals in other fields of research.

In a like manner this selection was determined by computing the citations to periodical literature of other journals in the 23 volumes of the *Journal of the Association of Official Agricultural Chemists*, believing that this was most representative of American agricultural chemistry. If one or more references are made to a magazine in 10 or more articles or discussions, the title appears in the table.

The table given serves a dual purpose: first, it ranks each publication according to its usage from 1915, the date of the *Journal of the A. O. A. C.*'s first issue, through 1940. And second, it shows the increase or decline in each journal's usage during the last ten years. After gathering these statistics, one thing in particular, which was unforeseen, becomes evident from the data. Some journals included herewith were published for a short interval only, and then ceased. It is quite likely that this sort of publication if very old may have little or no value to a research man. But yet there is a possibility that it will be of much import. Another influence is the fluctuation of the quality of the literature found in these journals. A change in policy of any of these publications may have altered their value and useful-

TABLE OF USAGE

Titles	*1915–40*	*1931–40*	*Titles*	*1915–40*	*1931–40*
Ind. Eng. Chem.	747	276	*J. prakt. Chem.*	19	8
J. Am. Chem. Soc.	448	241	*Z. anorg. Chem.*	19	12
Ind. Eng. Chem. Anal. Ed.	311	307	*Am. J. Sci.*	18	8
J. Biol. Chem.	285	141	*Ann. chim. applicata*	18	15
Cereal Chem.	212	100	*Chem. News*	18	6
C. A.	164*	95*	*J. Am. Med. Assoc.*	18	9
Z. offentl. Chem.	164	28	*Schweiz. Apoth.-Ztg.*	18	7
Analyst	158	98	*Apoth. Ztg.*	17	6
Ber.	144	85	*Pharm. Weekblad*	17	13
Z. anal. Chem.	123	60	*Pharm. Z.*	17	5
Biochem. J.	119	83	*Am. Chem. J.*	16	0
J. Am. Pharm. Assoc.	98	44	*Ann. chim. anal.*	15	3
Chem. Ztg.	89	42	*J. Nutrition*	15	14
J. Soc. Chem. Ind.	84	38	*Bodenk. u. Pflanzenernahr.*	15	15
Compt. rend.	80	50	*Rec. trav. chim.*	15	13
Biochem. Z.	79	50	*Chem. Weekblad.*	14	12
Z. physiol. Chem.	77	42	*Helv. Chim. Acta.*	14	12
Z. Untersuch. Lebensm.	66	50	*J. Wash. Acad. Sci.*	14	6
J. Chem. Soc.	59	32	*Pharm. Zentr.*	14	9
Ann. fals.	57	42	*Mikrochemie*	13	13
Am. J. Pharm.	56	31	*Proc. A. O. A. C.*	13	8
Angew. Chem.	56	29	*Cellulosechem.*	12	12
Soil Sci.	52	38	*Lancet*	12	2
Ann.	47	29	*Plant Physiology*	12	11
Science	45	35	*Wiss. Veroffent. Siemens-Konzern*	12	12
Bull. soc. chim.	44	21	*Z. ges. Brauw.*	12	9
Arch. Pharm.	42	20	*Z. physik. Chem.*	11	4
J. Am. Leather Chem. Assoc.	42	2	*Bull. inc. etud. ecole super. brass. Louvain*	11	5
J. Am. Soc. Agron.	42	41	*Can. J. Research*	11	11
Milt. Lebensm. Hyg.	34	24	*Facts About Sugar*	11	3
J. Agr. Sci.	33	20	*J. Inst. Brewing*	11	11
Pharm. J.	31	15	*J. Phys. Chem.*	11	4
Z. Wirtschaftsgruppe Zuckerind.	30	10	*Nature*	11	10
Chem. Zentr.	29	16	*Papier-Fabr.*	10	10
Monatsh.	27	26	*Z. Zuckerind. cechoslovak. Rep.*	11	1
Landw. Vers.-Sta.	26	12	*Ann. Phys.*	10	6
J. pharm. chimie	24	11	*Bull. assoc. chim. sucr. dist.*	10	7
Quart. J. Pharm. Pharmacol.	24	23	*Cotton Oil Press.*	10	2
Contrib. Boyce Thompson Inst.	23	23	*Proc. Roy. Soc. Series B.*	10	4
Am. Fertilizer	22	8	*Yearbook Am. Pharm. Assoc.*	10	9
Woch. Brau.	21	19			
J. Dairy Sci.	20	8			
Poultry Sci.	20	19			

* It is impossible to do justice to the *Chemical Abstracts* in this survey because it is perhaps the chief means of reaching periodical literature pertaining to chemistry. Almost every reference to the *Abstracts* appeared along with a reference to some rare foreign journal. This was to enable the reader to find the material at least in an abstracted form when the original was unavailable.

[1] GROSS AND GROSS, *Science n. s.*, **66**, 385–9 (1927).

[2] KAPLAN, *College and Research Libraries*, **1**, 241–5 (1940).

ness to a considerable extent. Therefore, in the table of statistics the number of references cited during the past ten years of the publication of the *Journal of the A. O. A. C.* is included as well as those from its first appearance to date.

In an effort to eliminate bulkiness, publications of state and government agencies have been omitted. The scope is limited to journals, bulletins, transactions, proceedings, etc., of societies and independent agencies.

With respect to the entries in this table, it should be noted that the generally accepted abbreviation of each title is used. Detailed bibliographical information regarding the publications may be found in *Chemical Abstracts*[3] and the "Union List of Serials."[4]

[3] *C. A.*, **30**, 8639 (1936).

[4] GREGORY, Editor, "Union list of serials in the libraries of the United States and Canada," checking ed., H. W. Wilson Co., New York City, 1939–40.

A History of the Match Industry[1]

M. F. CRASS, JR. *Washington, D. C.*

PART V—SAFETY OR STRIKE-ON-BOX MATCHES

THE almost universal use of white phosphorus for match-making purposes began to exert its insidious effect upon workers within the industry as early as 1839 (*1*). Although the subject of phosphorus necrosis will be fully dealt with in a subsequent article, mention of this terrible disease should be made at this point inasmuch as its appearance was directly responsible for the many efforts subsequently made to find a satisfactory substitute for white phosphorus in the match industry.

The discovery of non-poisonous amorphous phosphorus was made in 1844 by Anton Schrotter of Vienna (*2*). A short time later, Gustav Pasch of Sweden took out a patent for red phosphorus, which he believed to be an oxide of the element because of its preparation from white phosphorus by heating in a limited atmosphere. During the course of his experiments, Pasch found that a striking surface containing his new material would ignite matches that did not contain white phosphorus, but contained instead substantial amounts of active oxidizing agents. Although his patent clearly enunciated the principle concerning use of red phosphorus in striking surface compositions, Pasch made no apparent effort to develop his invention further.

In 1845 Professor R. Böttger of Frankfort-on-Main suggested a similar procedure independently of Pasch (*3*). The next few years saw the production of many types of safety matches based upon this principle, but they were mainly unsuccessful because of the hygroscopic character of the composition, coupled with its tendency to explode when struck on the prepared surface. The lack of pure amorphous or red phosphorus was also a handicap.

In 1851 an improved process for preparing red phosphorus was developed in England (*4*), and in 1855 the first successful safety or "hygienic" match was produced at Jonköping, Sweden, by J. E. Lundstrom. Lundstrom's patents included methods as well as formulas, and were quickly purchased in other countries by match manufacturers. Use of the new safety matches rapidly increased, aided by legislation in many European countries which regulated or prohibited the use of white phosphorus in match manufacturing, and today 80 per cent of all matches used abroad are of this type. In England alone, the total output of safety matches in 1856 was in excess of 40 million units.

Many attempts were made to substitute harmless red phosphorus for the poisonous white variety in friction match compositions but with little success, principally because of poor moisture-resistant qualities in the resulting matches, and the difficulties experienced in drying them.

"Allumettes Androgynes" were introduced in France in 1859 (*4*). These consisted of double-headed matches, one head made up of a potassium chlorate composition and the other head of a red phosphorus paste. To obtain a light the splint was broken in the middle and the two heads rubbed together. A similar match was patented by Moore in the United States in 1865 (*5*). This idea reasserted itself as recently as 1919 when a Canadian patent was granted for a match with two heads (*6*).

Several early patents were taken out in the United States for safety matches prepared for use without the aid of a red phosphorus striking surface. A patent granted to a Swede named Hjerpe specified potassium chlorate, bichromate of potash, iron oxide, and glue in the match head, while the "rubber" or striking surface was compounded from antimony sulfide, bichromate of potash, lead oxide, and glue (*7*).

While very popular in Europe, the safety match was not used to an important degree in this country until about 1920. An early (1877) account of the preference of the American public in this respect, and one which also throws additional light on the early parlor type of friction match follows (*8*):

"An American prefers to put his hand into his pocket, take out a match and strike it on his pantaloons or shoe to economizing by carrying them around in the box in which he buys them. And you could never get the Irish servants here to use them unless you had the priest on your side. In many cases when a safety match is struck some of the phosphorus on the box flies off and gives rise to danger of fire on carpet, floor, or seat. The safest matches are those requiring considerable friction for ignition and are, for the most part, generally found with a considerable amount of sulphur in the heads. They are quiet, and upon lighting do not scatter any part of the head about. But they kindle slowly and the

[1] Continued from the June, 1941, issue.

sulphurous fumes are objectionable. They can also be lighted so conveniently by rubbing on the wall that a great temptation is held out to servants to disfigure the appearance of a room in this way.

"About twenty years ago parlour matches were introduced and have rapidly grown in favour. They are free from odor and ignite conveniently and rapidly. Their noisy explosion is occasioned by chlorate and may be prevented by substituting nitrate of potash. Our matches are superior to the German because they are not coated with varnish. They are most popular in the west, south, and among the wealthy. They are similar to the safety match in that if coated too profusely with composition they will fly and scatter to some distance. They take fire easily when stepped upon and must be kept from children. Insurance companies, however, make but little distinction in their rates between parlour matches and the other types. Fires may result from the overturning of a box by a dog or cat, or by the gnawing of the tips by rats or mice."

Formulas for a number of commercially made safety matches, including the Jonköping match, are reproduced in the following table:

EARLY COMMERCIAL SAFETY MATCH FORMULAS

Material	*Jonköping*	*English 1902*	*English 1902*	*American 1902*	*Capetown*	*American*	*Friction for Boxes*
Glue	12	8.5	8	5.4	1.5	7	..
Gum arabic	3	3	11.5	..	1.5	3.5	4
Gum tragacanth	..	1	1.5	0.3	..	0.3	..
Potassium chlorate	108	67	50	35	20	60	..
Potassium bichromate	3	..	3.7	..	0.5	0.7	..
Manganese dioxide	6	..	3.8	..	0.5	2.2	30
Sulfur	16	2	1.4	1	2	3.5	..
Burnt umber	16	..	2.8	..	0.5	5.5	1
Ground glass	28	14	8.3	9.4	5	8.5	6
Diatomaceous earth	..	2	2	1	..	..	..
Barium chromate	..	3.8	..	2	1.3	3.3	..
Lead thiosulfate	..	1	..	1.5	..	1.5	..
Zinc oxide	..	1	..	0.5	0.5	1.7	..
Venetian red	..	..	5	..	..	..	..
Rosin	..	..	..	0.5	..	..	..
Asbestos, fine	..	..	..	..	1.3	..	..
Red phosphorus	..	..	..	..	..	..	35.3

A "safety blazing fusee" with a single tip, differing from the usual double-dip fusee in that it required a prepared surface for ignition, was patented by Schneider in 1874 (*9*). According to the inventor, the composition "rendered the fusee inextinguishable in rain or wind and will not poison anybody should the composition by accident or through carelessness be eaten." The formula contained the following ingredients: glue 2, starch 10, golden sulfide of antimony 8, powdered glass 20, potassium chlorate 48, pumice 10, saltpeter 12, cascarilla bark 4, and lampblack 2. The striking surface contained starch, red phosphorus, and black sulfide of antimony.

Headless safety matches were first patented in this country in 1889 by John Lutz (*10*). Lutz attempted to exploit his invention by pointing out that no dipping frames were required in the preparation of his matches. A number of patents were granted in 1900 and 1901 for such matches, procedure in most cases consisting of boiling the wood splints in a concentrated solution of chlorate and caustic (*29*).

A patent granted in 1922 outlined the following procedure (*11*). Boil wooden splints in an aqueous solution of potassium chlorate and dry. Then soak the tips in a concentrated solution of barium chlorate and dextrine, dry, and treat the matches once again with a saturated solution of potassium chlorate.

PART VI—DOUBLE-DIP FRICTION MATCHES

Many of the vesuvians or wind matches already described (*12*) were made with two heads, the large pear-shaped bulb or under-head containing large quantities of slow burning materials such as powdered charcoal or wood flour, designed to provide a relatively long burning, generous flame that would be sustained even in high winds or heavy rains. Application of the double-dip principle to friction match manufacturing as it exists today was first made by Frederick W. Farnham, who in 1888 was granted a patent (*13*) for a double-dip match "which will be practically safe in use and yet will be capable of ignition upon any convenient surface." In applying for his patent, Farnham wrote as follows:

"The ordinary parlor match in use consists of a thick, heavy splint, tipped with a large round head of inflammable material. When struck sharply upon a frictional surface, it is well known to all that particles of the head are liable to be thrown off in any direction, and as these particles are always ignited, they are dangerous to the person or dress of the person that lights them. Such matches are often struck upon gas brackets on a level with the eyes, which are thus put in danger from the flying particles. Again, such matches, if stepped on carelessly, will ignite directly with a large flame, dangerous to the dresses of ladies and always a source of risk."

Farnham utilized for the base or bulb of his matches a non-phosphorus composition incapable in itself of taking fire through friction on an ordinary surface. For the small tip, he utilized a phosphorus-bearing compound.

Although the double-dip match did not come into extensive use until shortly after the patent expired in 1905, it was one of the principle factors in reducing the number of accidental fires due to matches. Matches of this type could be boxed without danger of the sensitive phosphorus-containing tips rubbing against each other. The invention is therefore considered to be one of the more important developments in the history of the friction match. All of the strike-anywhere matches used today are patterned after Farnham's original double-dip principle.

A modification of Farnham's patent was proposed by Sommers (*14*) in 1905, who pointed out that the inert base or bulb of Farnham's match would often fail to take fire from the sensitive phosphorus-containing tip because of its lack of sensitivity. Sommers therefore added a small amount of phosphorus to the base composition, which eliminated the tendency of Farnham's match to "burn over the head" without evolution of flame. Sommers' base composition consisted of potassium chlorate, glue, phosphorus, rosin, plaster of Paris, whiting, flint, and coloring material. His tip composition contained phosphorus, glue, flint, plaster, zinc oxide, and color. The following account from Sommers' patent specification gives an excellent description of both the sulfur and parlor matches in use at that time:

"The sulphur match is objectionable because of the smell and the fumes given off from it, and is also objectionable because of the long period of time which is required to ignite it, the ordinary sulphur match requiring several seconds before the heat has reached a degree to ignite the stick. On the other hand, the match which is commonly known as the 'parlor match' has a terminal composed largely of chlorate of potash—that is—one which ignites quickly and readily on any friction rubbing surface, but with detonating force. Because of the detonable character of the compound, it is quite dangerous to use. Flying particles sometimes produce serious injury to persons standing nearby, by striking the face or eyes and burning through the skin or injuring the eyes. Such flying particles of the ignited material also often set fire to drapery and other nearby combustible material. A further serious objection to this kind of match is the noise which attends the striking and ignition. Another serious objection arises from the fact that the compound deteriorates rapidly and after a few months time the match has deteriorated to the extent that it will frequently fail to set fire to the stick."

Efforts to reduce the danger of fires caused by the heads of matches rubbing against each other in boxes had been made prior to the invention of the double-dip match, however. Perhaps the first of such attempts was that of J. R. Dey who, in 1863, was granted a patent for a splint with a pointed tip (*15*). This splint, shaped like a sharp-pointed lead pencil, was tipped with a white phosphorus composition at the point. The inventor claimed that not only were fire hazards reduced because the tips could not rub against each other, but also by reducing the amount of composition safety in their manufacture was facilitated.

PART VII—NON-POISONOUS FRICTION MATCHES

Because of the popularity of the strike-anywhere friction match in this country and the equally popular aversion to the safety match that had been accepted so widely abroad, many attempts were made to develop a satisfactory easy-striking non-poisonous friction match to take the place of the poisonous white phosphorus match in general use throughout the United States.

In 1860, Puschen of Nuremburg produced a red sulfide of phosphorus which he proposed as a substitute for white phosphorus in match manufacturing. Nothing came of this proposal, probably because of the difficulties experienced in producing a pure and stable compound, and also because of the additional expense involved. With the number of cases of phosphorus necrosis becoming greater and more widespread, experimenters redoubled their efforts to discover a satisfactory substitute for white phosphorus, and many compounds were utilized experimentally in compositions containing relatively large amounts of potassium chlorate. The most promising of these appeared to be various lead compounds, particularly the cyanide, thiocyanate, and hyposulfite. Typical formulas follow:

Material	*Formula No. 1*	*Formula No. 2*	*Formula No. 3*
Potassium chlorate	90	5	28.5
Potassium bichromate	45	8	3
Lead peroxide	25	3	..
Red lead	20	..	..
"Oxysulphuret of antimony"	20	0.5	..
Antimony sulfide	15	..	..
Ground glass	15	8	10.5
Potassium cyanide	5	..	..
Lead cyanide	..	8	..
Lead nitrate	..	..	2.5
Gum	55	8	?

In 1869 a patent (*16*) was granted covering the use of red phosphorus, flour, potassium chlorate, and glue. The inventor first charred the ends of the splints, then dipped them in molten paraffin, followed by application of the above composition. To please users with sensitive tastes, the composition was given a pleasant color and odor with the use of a pigment and cascarilla bark.

Use of lead hyposulfite in match compositions was introduced in 1870 (*30*). Thirty-five parts of this material were used in conjunction with 20 of potassium chlorate, 15 of ground glass, 3 of glue, and one each of potassium bichromate, manganese dioxide, and lead peroxide.

In 1872 the use of "phosphide of sulphur" in place of phosphorus was patented by F. Zaiss, who deplored the dark and unattractive match heads currently in use and suggested that attractive colors be imparted to the match heads through the use of light-colored materials (*17*). Zaiss used, in addition to his phosphide, potassium chlorate and lead nitrate, perfuming the composition with gum benzoin, cascarilla bark, or cinnamon. This is the first recorded instance of the use of a non-poisonous sulfide of phosphorus, although it was apparently unsuccessful and did not result in commercial adaptation until the utilization of the sesquisulfide by Sevene and Cahen in 1898 (*18*).

From 1890 on, many applications for patents relating to non-poisonous friction matches were submitted to the patent office, in a determined effort to establish a satisfactory substitute for white phosphorus, the terrible results of which were making themselves manifest in increasing numbers of necrosis cases. In 1899 Bahy was granted a patent (*19*) for friction matches "which ignite more easily by friction than do the matches that have heretofore been made containing phosphorus." Bahy's formula contained calcium hypophosphite, glue, turpentine, potassium chlorate, barium chromate, ground glass, and aniline yellow. In the same year, Hackel was granted a patent (*20*) for a friction match containing potassium bichromate, gum arabic, red phosphorus, potassium chlorate, and lead thiosulfate. Still another non-poisonous formula contained chlorate 200, glass 100, whiting 60, red phosphorus 50, plaster 35, and glue 65. As previously explained, this type of match was never commercially successful, due to the difficulty experienced in drying match heads containing red phosphorus.

In 1900 a patent was issued to Jones for a non-poisonous friction match containing potassium chlorate, antimony sulfide, a metallic thiosulfate, manganese dioxide, potassium bichromate, red prussiate of potash, and glue (*21*). Another formula contained chlorate, antimony sulfide, lead peroxide, powdered charcoal, potassium xanthate, nitronaphthalene, cyanogen persulfide, and persulfocyanic acid (*22*).

Patents taken out between 1902 and 1905 include the following: use of a barium salt of a polythionic acid in combination with potassium chlorate (*23*); use of a sulfopolythionate with an oxidizing agent (*24*); a combination of chlorate, sulfur, antimony sulfide, and

anhydrous diazobenzenesulfonic acid (*25*). In 1903 William Muir introduced the non-poisonous scarlet phosphorus to friction match manufacturing, using it in conjunction with potassium chlorate (*26*). In 1905, Staier patented the use of scarlet phosphorus in conjunction with chlorate, sulfur, plaster of Paris, zinc oxide, whiting, and glue (*27*). Scarlet phosphorus is more reactive chemically than either red phosphorus or phosphorus sesquisulfide, being intermediate in activity between the red and yellow allotropic forms of the element.

The many proposed substitutes for white phosphorus were not commercially successful to any important degree and did not materially reduce the production and consumption of poisonous friction matches in the United States. The substitutes were either too expensive, or they could not be obtained commercially in a sufficiently pure form to meet the requirements of the industry. With the possible exception of scarlet phosphorus, none of the substitutes or formulas suggested were of sufficient sensitivity even to approach the smooth and easy striking characteristics of the white phosphorus match, and scarlet phosphorus was too expensive to use except in a very small way.

It remained for two Frenchmen, Henri Sevene and Emile David Cahen, to solve the problem effectively in 1898 and to make the most outstanding contribution in the history of the industry to chemical firemaking. Their achievement consisted in the successful application of the non-poisonous phosphorus sesquisulfide to friction match manufacturing (*18*). A detailed account of the introduction of the sesquisulfide will be given in a subsequent paper.

According to a patent issued in 1903 (*28*), it was widely believed that the presence of free phosphorus as an impurity was necessary in the sesquisulfide in order to make the latter function effectively in match composition; the inventor further stated that the type of sesquisulfide available was unstable and contained an objectionable amount of free phosphorus. The patentee claimed the "discovery" that the presence of free phosphorus in the chemical combination of phosphorus and sulfur was not necessary, and that the available impure sesquisulfide could be replaced for match purposes by other sulfides of phosphorus that were easier to prepare in pure form. Successful application of the sesquisulfide was immediate, however, and although it was not used in the United States until years afterward for reasons that will be subsequently explained, it became extensively used for friction matches in both England and France as early as 1900.

WHITE PHOSPHORUS FORMULAS USED BY AMERICAN MATCH COMPANIES PRIOR TO 1910

Parlor Match

Glue	35 lb.
Chlorate	58 "
Rosin	7½ "
Plaster	10 "
Flint	21 "
Whiting	27 "
Phosphorus	10½ "
Color	Fuchsine (or walnut brown)

Sulfur Matches

Glue	50 lb.
Whiting	70 "
Phosphorus	33 "
Neutral blue	10 "

Silent Parlor Match

Gum arabic	15.3 lb.
Glue	1.5 "
Phosphorus	5.5 "
Red lead	56.1 "
Nitric acid	21.4 "
Color	None

Parlor Match (Detroit)

Irish glue	30 lb.
Chlorate	60 "
Rosin	7 "
Plaster	12 "
Flint	23 "
Whiting	27 "
Phosphorus	10 "
Color	—Fuchsine —Walnut brown —Acid pink —Victoria blue

Parlor Match (Ives and Judd)

Antimony sulfide	1 lb. 14 oz
Phosphorus	7 " 14 "
Crocus metallorum	9 " 13 "
Chlorate	41 " 0 "
Flint	40 " 8 "
Glue	29 " 0 "

Parlor Match (Swift and Courtney)

Glue	31½ lb.
Chlorate	50 "
Red antimony	9 "
Zinc oxide	5 "
Flint	55 "
Phosphorus	8¾ "
Color	Walnut brown

Sulfur Matches (Oshkosh)

Glue	65 lb.
Whiting	65 "
Lamp black	¼ "
Turpentine	1 qt.
Phosphorus	25 lb.
Color	Rosaniline

NON-PHOSPHORUS FORMULAS

Blazer Composition

Gum arabic	10.5 lb.
Glue	0.7 "
Red phosphorus	0.6 "
Chlorate	27.5 "
Diatomaceous earth	2.9 "
Cascarilla	1.4 "
Incense	1.4 "
Ground glass	55.1 "

Tapers for Vestas

Stearin	80 lb.
Paraffin wax	21 "
Gum damar	6 "
Carnauba wax	5 "

(To be continued.)

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The Polarographic Method of Analysis

V. Applications

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FROM a study of Parts III[1] and IV[2] of this series it would appear that the number of applications of the polarographic method were infinite. Indeed at one time it was thought possible that the polarograph might some day in many instances replace the analytical chemist. This was not so absurd in view of the excellent reproducibility, the high sensitivity, and other outstanding features of the method, such as rapidity of operation, simultaneous quantitative and qualitative analysis of several components of a solution, the fact that in most cases the solution remains unaltered during the analysis and can be used for other purposes, the possibility of analyzing quantities the size of a drop, and the automatic graph which provides a permanent record of the analysis. Unfortunately there are but few practical analyses in which are found the ideal conditions necessary to make use of all these features. Many analyses with the dropping mercury electrode become so complicated that it is best to use a different method. Most analyses that are feasible polarographically require a careful combination of electrochemical and general analytical procedures by a well-trained chemist. This does not detract from the value of polarography, because it has a distinct usefulness for numerous problems, as is generally recognized today. Thus it serves its purpose along with colorimetry, spectroscopy, potentiometry, and other specialized methods of analytical chemistry.

Up to the present, no systematic procedure for quantitative and qualitative polarographic analysis of an unknown has been worked out. A few special analyses published in adequate detail are available but even these should be used with reservation by either novice or expert. With few exceptions, therefore, every contemplated polarographic analysis presents its own problem for which the investigator must develop his own technic. A clear understanding of the fundamentals which have been described in the preceding articles should make this possible. This paper is intended to call attention to the difficulties and limitations involved in practical analyses, and to point out some of the means to overcome these difficulties. In addition, some of the less obvious, mostly empirical applications of polarographic principles will be mentioned.

APPLICATIONS IN GENERAL

To be suitable for polarographic analysis a substance must be electro-reducible or -oxidizable within the range of the electrode, it must be in true solution, and it must be stable for the duration of the measurement so that a pure diffusion current, as defined in Part III,[1] can be obtained. In the case of the dropping mercury electrode, the potential range is from $E_{S.C.E.}$ $+0.6$ to -2.6 volts under optimum conditions. Some substances known to be reducible by hydrogen, such as oleic acid, are not reduced within this range of potential. A prediction about the electro-reducibility of a substance can therefore never be made with certainty, and an actual test will always be necessary.

The analyses are carried out most easily if the material to be analyzed is in a concentration of 10^{-4} to 10^{-3} molar and the volume of solution is 5 to 20 cc. In extreme cases 10^{-6} M solutions and volumes of 0.005 cc. can be analyzed. Special precautions are then necessary, because the quantity of material which is removed by electrolysis and also the end-products formed become significant under these conditions. One can calculate that quantities as little as 0.001 γ should still be determinable; one microgram may be considered the practical limit of the method. If carried out with volumes of solution exceeding one cc., the accuracy of quantitative analysis is often as high as one per cent. This is possible by repeating analyses of the same solution several times and averaging the results. Individual analyses are usually accurate to about five per cent; when made under extreme conditions they are probably not better than twenty per cent.

As a rule, results obtained with this method are evaluated comparatively rather than absolutely. As has been shown before,[1, 2] absolute measurements are certainly feasible, but special precautions must be taken to insure the proper conditions. In practice it is simpler to prepare calibration curves similar to Figure 5 of Part III[1] and use these for comparison. Since there have been instances in which preceding reductions at the dropping mercury electrode have influenced the wave-height of subsequent reductions, synthetic mixtures with a composition approximating that of the unknown should be prepared and electrolyzed *in the same medium* as that used for the analysis. If no thermostatic control is available, the temperature coefficient of the calibration curve should be determined so that corrections can be made. The supporting electrolyte (Grundlösung) does not have to be perfectly pure; a preliminary "blank" curve will indicate the current due to impurities which must be subtracted from the "test" curve. If the unknown is more concentrated than 10^{-3} M, it is usually possible to work with the solutions open to air. Naturally the current of the oxygen wave must also be subtracted

[1] J. CHEM. EDUC., **18**, 172 (1941).
[2] *Ibid.*, **18**, 227 (1941).

from the "test" curve. In more dilute solutions, the atmospheric oxygen must be removed before analysis by physical (inert gas) or chemical (sodium sulfite or manganous chloride) means.

The following is another basis for comparative analyses which is especially suitable for isolated determinations: To the unknown add a small quantity of a solution containing the same ion in a known concentration. Calculate the original concentration of the unknown from the increase in wave-height corrected for the new volume. The concentration of the unknown X must be proportional to the wave-height h;

$$X = kh \tag{1}$$

Adding n cc. of the known solution with concentration C to m cc. of this unknown produces a new wave-height, H, so that

$$\frac{mX + nC}{m + n} = kH \tag{2}$$

From this we can calculate that the concentration

$$X = \frac{-nCh}{mh - H(m + n)} \tag{3}$$

The selection of a suitable supporting electrolyte is of great importance in polarography. Hohn[3] has listed a number of these with recommendations for their use. Most laboratories will develop their own slightly modified Grundlösung for their particular problems. Figure 1 may be of help in estimating the range of potential for which the supporting electrolyte is applicable. In this chart, some of the most frequently used cations and those anions which form complexes with mercury are listed in concentrations ranging from 1 M to 10^{-5} M. While the values given here are not very accurate, they show us, *e. g.*, that in a solution of 1.0 N sodium cyanide polarographic analyses could only be carried out between $E_{S.C.E.}$ -0.5 and -1.9 volts. We also see from Figure 1 that, in spite of the high overvoltage at a dropping mercury electrode, reductions at potentials more negative than $E_{S.C.E.}$ -1.0 volt cannot be carried out in strong acid solutions.

Granted that organic and inorganic substances have reduction potentials by which they can be characterized, it is obvious that even in the maximal potential range, the reduction potentials of several hundreds of substances must in many instances overlap or come so close together that their resolution is impossible. Even when the much smaller number of inorganic ions is considered, wave coincidences occur under optimum conditions of relative concentrations. These coincidences may sometimes be abolished by changing the pH of the solution or by forming suitable complexes but often the analysis may still be impossible if an ion with a more positive reduction potential is present in excess.

To demonstrate the need for separation and for a favorable relation of the heights of individual waves, Figures 2 and 3 were prepared. The curves shown

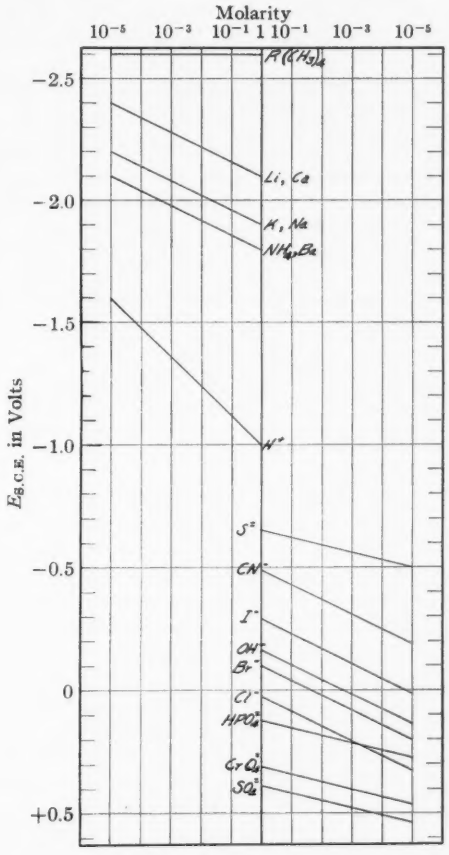

FIGURE 1.—DIAGRAM FOR CALCULATING POTENTIAL RANGES OF DIFFERENT SUPPORTING ELECTROLYTES

are theoretical current–potential[2] curves of two reversible reductions at 30°C., calculated for a two-electron

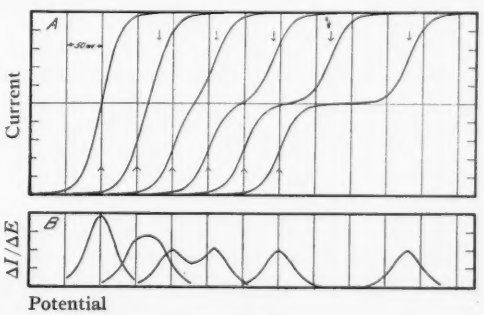

FIGURE 2

(*A*) Theoretical current–potential curves of two waves of equal height whose half-wave potentials (indicated by arrows) are separated by 0, 30, 60, 90, 120, and 180 millivolts

(*B*) $\Delta I/\Delta E$ of the above curves plotted against potential

[3] HOHN, "Anleitung für die chemische Laboratoriumspraxis," Vol. III, Julius Springer, Berlin, 1937.

change[4] per molecule. Since these are current–*potential* curves they are independent of the actual scale of the current axis, *i. e.*, the curves should look the same whether the sum of the two waves were 10 or 1000 microamperes. It is questionable, however, that such ideal

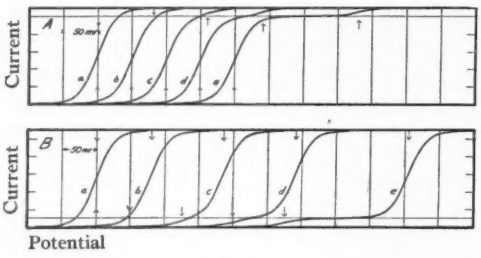

FIGURE 3

Theoretical current–potential curves of two waves whose half-wave potentials (indicated by arrows) are separated by 0, 30, 60, 90, and 180 millivolts. The heights of these waves are in a ratio of (*A*) 10:1 and (*B*) 1:10

curves can be obtained in practice, since the observed current–*voltage* curves cannot be corrected for *IR* with sufficient accuracy if the currents are large.[2] In Figure 2, the ratio of the two curves is unity; in Figure 3, the more positive curve is ten times as high as the more negative curve in the upper series *A*, while the opposite is true in the lower series *B*.

The half-wave potentials of the curves of Figure 2 are indicated by arrows. They are separated by 0, 30, 60, 90, 120, and 180 millivolts, respectively. It may be seen that a difference of at least 90 millivolts between the half-wave potentials is necessary to produce measurable waves. If the difference is only 30 millivolts, the waves overlap to such an extent that a determination of wave-heights becomes impossible. A separation of 60 millivolts in this case is just enough to see that there are two inflections, but no accurate measurements can be made. If the change of current per unit change in potential, $\Delta I/\Delta E$, is plotted against the potential, as in the lower part *B* of Figure 2, a sharp peak will be obtained at the half-wave potential of each wave. In a double wave, two such peaks will be obtained if the waves are separated sufficiently. These increment ratios are often used in potentiometry (see Part I[4]) but so far have not been adapted to polarography. It seems likely that a detailed study of this type of curve analysis may be of value for the determination of half-wave potentials and wave-heights.

Curves with similar separations of the half-wave potentials, but with a less favorable ratio of the two waves, are shown in Figure 3. It may be observed that even at a separation of 90 millivolts, the measurement of the waves is somewhat difficult if the more negative wave is smaller than the one occurring at more positive potentials. In the reverse situation the first curve can be magnified by increasing the galvanometer sensitivity; it can then be measured with a smaller error.

These same Figures 2 and 3 can be used for a consideration of reactions involving one electron per molecule, by doubling the scale of the abscissa. We then find a minimum of 180 millivolts for satisfactory separation of half-wave potentials. This leads us to the general conclusion that for measurements of simultaneous reductions the midpoints of waves must be separated by at least $RT/nF \ln 1000$.

One of the most important questions faced by every worker in polarography is how to measure wave-height. The literature is confusing and of little help, for a number of empirical methods have been proposed by different authors. These are not generally applicable but, if used consistently, give satisfactory results in the particular analyses for which they were designed. Only the three most popular methods will be mentioned here; they are demonstrated in Figure 4. To test them, two sets of theoretical current–potential curves (corresponding to half-wave separations of 90 millivolts in Figures 2 and 3) have been drawn. The upper set (Figure 4*A*) represents conditions in which the residual current is negligible, as may occur when large currents are being plotted.[1] The lower set (Figure 4*B*) shows curves in which the residual current becomes appreciable compared to the diffusion

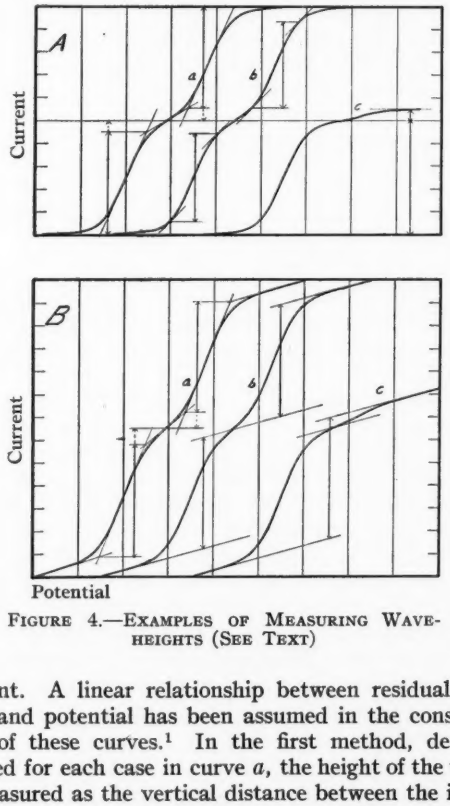

FIGURE 4.—EXAMPLES OF MEASURING WAVE-HEIGHTS (SEE TEXT)

current. A linear relationship between residual current and potential has been assumed in the construction of these curves.[1] In the first method, demonstrated for each case in curve *a*, the height of the wave is measured as the vertical distance between the intersections of the projections of the straight portions of

[4] J. CHEM. EDUC., **18**, 65 (1941).

the curve. In the upper set of curves this method would lead to low results and give us an erroneous half-wave potential, while more correct results would be obtained in the lower set of curves. A modification of this procedure, in which half of the current increase during the plateau is added to the height, would give erroneous results in the lower set but correct ones in the upper set of curves. Either procedure is difficult to use in measuring curves of type *c* (Figure 4). A second method consists in placing tangents to the curves at an angle of 45° and measuring the vertical distances between the points of contact. This is demonstrated on the upper curve *b*. It will give erroneous results for the wave-height but will give correct information about the half-wave potential in both sets of curves. The third method requires considerably more experience but it is the most reliable known method and is certainly to be recommended. In this method the residual current is extrapolated and thus automatically eliminated.[1] Lines are then drawn parallel to this through the midpoint of the plateaus. With some experience it is possible to draw these lines without much difficulty. If necessary, a combination of extrapolating, as described in the first method, will help locate this midpoint. It may be seen that by this third method the diffusion currents measured are identical with the theoretical values (curves *c* and lower curve *b*, Figure 4). For this reason it seems that the determination of wave-heights for use in the Ilkovič equation[1] is advisable only with the third method.

Next we will consider what point in the oscillations of current occurring with each growing drop of mercury should be taken for the analysis. The Ilkovič equation of the diffusion current[1] considers a mean current during the growth of each drop. Many workers have, therefore, drawn their lines halfway through the recorded oscillations in the polarograms. This is not necessarily correct because, as shown in Part II,[5] the galvanometers used are so slow that they cannot follow the growth of current with the growth of drops and will, therefore, indicate at their maximum deflection a current which may be close to the mean. No detailed studies have been made to settle this point, but since the "mean" method and that of using maximum galvanometer deflections show agreement with the Ilkovič equation, either one is practicable. In this connection it should be pointed out that a comparison based on the Ilkovič equation of diffusion current data obtained by different authors can only be made if the galvanometers used have the same period of swing in relation to the drop-time. Otherwise, no perfect agreement can be expected.

If the residual current becomes very large compared to the diffusion current, the latter can only be measured if the former is eliminated by an empirical compensation method such as that developed by Ilkovič and Semerano.[6] Also, deflections of the galvanometer due to large diffusion currents may in some instances be compensated by connecting a second circuit to the galvanometer and passing an opposing current through it. In this way small currents occurring at a more negative potential (Figure 3*A*) can be measured with greater galvanometer sensitivity. The reliability of this procedure must of course first be established in each individual case. Unfortunately, oscillations of the galvanometer are thus magnified and complicate the current measurement. To overcome this difficulty, Neuberger[7] has placed a condenser of about 3000 microfarads across the galvanometer. Lingane and Kerlinger[8] have discussed this procedure in greater detail.

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These may best be discussed by a consideration of Figure 5, where most of the known half-wave potentials of the inorganic ions are represented. These values have been taken from a recent tabulation of Heyrovský.[9] They are referred to the saturated calomel electrode and should only be considered as close approximations, since it is known that they vary depending on the ionic strength of the solution. As has been shown,[2] activities should be used instead of concentrations to make the potential equation accurate. This would necessitate a consideration of ionic strength for the calculation of half-wave potentials at unit activity.

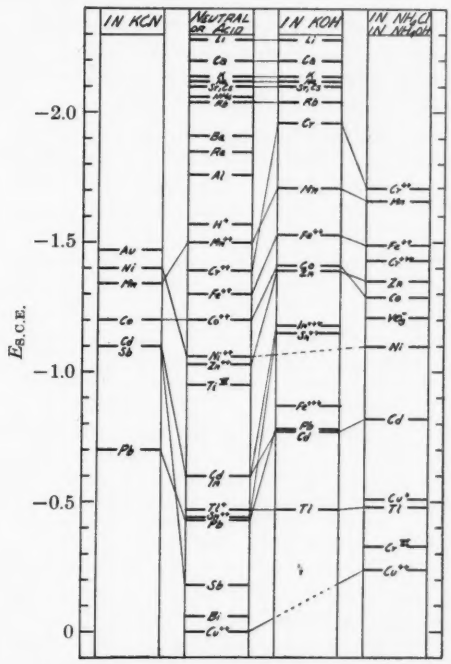

FIGURE 5.—TABLE OF HALF-WAVE POTENTIALS OF METAL IONS

[5] J. CHEM. EDUC., **18**, 111 (1941).
[6] *Collection Czechoslov. Chem. Commun.*, **4**, 176 (1932).
[7] *Z. anal. Chem.*, **116**, 1 (1939).
[8] *Ind. Eng. Chem., Anal. Ed.*, **12**, 750 (1940).
[9] *Collection Czechoslov. Chem. Commun.*, **11**, 586 (1939).

In Column 2 are shown the potentials obtained in neutral or weakly acidic solution. Many of these are so close together that a simultaneous estimation would be impossible. In this case it is necessary to remove one of the components chemically, or to change the components into complexes, from which they deposit at potentials far enough apart so that each wave can be measured separately. In practice this is of great importance, but a warning should be given that the wave-height of the complex is not necessarily identical with the wave-height of the free (hydrated) metallic ions, since their diffusion coefficients may differ. The half-wave potentials of a number of complexes are also shown in the diagram. Column 1 shows the potentials obtained in 1 *N* potassium cyanide, Column 3 those in 1 *N* potassium hydroxide, and Column 4 those obtained in a solution which is 1 *N* with respect to ammonia and ammonium chloride. The connecting lines show clearly some of the possibilities of separation. For instance, a mixture of nickel and zinc, the curves of which overlap in neutral solutions, will produce two waves separated by 250 millivolts in the ammonium buffer. The reduction of thallium and cadmium ions in neutral solution shows waves which are 130 millivolts apart and can be measured easily if the concentration ratio is favorable. Their separation is definitely improved in the ammonium buffer, where it is 330 millivolts. Judging from the chart a similar separation should be possible in 1 *N* potassium hydroxide but, as will be shown, the cadmium wave is almost completely lost in the alkali. Analysis in 1 *N* potassium cyanide would only give the cadmium wave because the thallium wave is outside the range of measurable potentials, as can be seen from Figure 1. These conditions are best demonstrated by the following experiment carried out with the apparatus described in Part II.[5]

Experiment 1.—Electrolyze, air-free, between −0.3 and −0.9 volt, a solution of 10^{-4} *M* thallous sulfate and 10^{-4} *M* cadmium sulfate in (*a*) 0.1 *N* potassium chloride, (*b*) 0.5 *M* ammonium chloride plus 0.5 *M* ammonium hydroxide, and (*c*) 1 *N* potassium hydroxide. Use the galvanometer shunt at position No. 5 and a saturated calomel half-cell as anode.

The results are shown in Figure 6 together with the automatically recorded polarograms of the same solutions. We see that the thallium half-wave potential is fairly constant in all three solutions while that of the cadmium is displaced to more negative values in solutions *b* and *c*. The ammonium solution is only half as concentrated as required for Figure 5, hence the separation of the half-wave potentials is only about 300 millivolts. Note that the wave-heights of the two components are different in the three solutions. While this difference is not so marked with thallium, it is very striking in the case of the cadmium wave, which almost disappears in the hydroxide. Curves *a* and *c* of this figure may serve as good practical examples of the limiting half-wave potential differences and concentration ratios during the simultaneous analysis of two ions. Similar limiting conditions in potentiometric titrations have been shown in Figure 3*C*, Part I.[4]

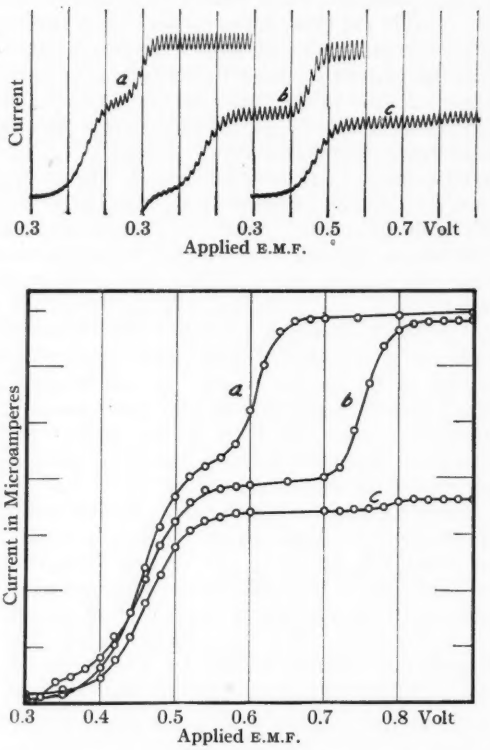

FIGURE 6

Current–voltage curves of 10^{-4} *M* thallous sulfate and 10^{-4} *M* cadmium sulfate in (*a*) 0.1 *N* potassium chloride, (*b*) 0.5 *M* ammonium chloride plus 0.5 *M* ammonium hydroxide, and (*c*) 1 *N* potassium hydroxide. Upper set of curves obtained with automatic polarograph, lower set obtained manually

It is impossible to mention here any of the numerous special applications for which detailed analyses have been worked out. These may be found indexed in *Chemical Abstracts* under the title of Polarography. As to a general procedure the following may be recommended:

Carefully weigh out a sample of material and bring it into solution by suitable means. Following this, dilute to a known volume and analyze aliquots polarographically in a variety of supporting electrolytes whose "blank" curves have previously been determined. The addition of the unknown solution to the Grundlösung should be made in small steps until a cursory inspection of the resulting polarogram shows that the wave-heights obtained are easily measured and well defined. Further additions are to be avoided because some of the waves might be made to overlap. A comparison of the observed half-wave potentials with those given in Figure 5 should make a qualitative analysis possible. If there is any doubt, a confirmatory test can be made by adding a known amount of the substance in question to the

solution and noting the increase in the wave which is studied, remembering that the addition of this known amount brings about an increase of the total volume. The observed wave-heights are compared with calibration curves which have been prepared under very similar conditions in such a way that the percentage concentration or the absolute quantity of the substance can be read off directly. It happens frequently that the linearity of such curves does not hold for very low concentrations; extrapolations in that region are therefore not permissible.

If the composition of the sample is approximately known, a more detailed procedure can be followed. By a preliminary separation the easily analyzable components are grouped together in several solutions for polarographic analysis and the remainder of the sample is retained for analysis by a different method.

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In applying the polarographic method to organic analyses, even greater difficulties are encountered than in the inorganic field. This is due to the fact that most organic unknowns are so much more complex, and that even if a fairly simple and relatively pure solution is available, the resulting curves may be complicated because the reduction is irreversible or goes on in several steps. The number of practical applications has therefore been small and most of the studies have been of a theoretical nature. A list of organic compounds investigated up to 1938 has been prepared by Müller.[10] While most of these electrolyses have been carried out in aqueous solutions, some were performed successfully in weakly conducting organic solutions. In general it seems advisable for a quantitative analysis to have the unknowns prepared in such a way that only one of the constituents is determined at a time. This does not preclude the occasional simultaneous analysis of several organic compounds.

Some of the most informative experiments have been carried out on reversible organic oxidation-reduction systems in which the end-products were known with as much certainty as the starting material. Since many organic substances are weak acids or bases, their reduction potentials shift with the pH, and sufficient buffering becomes of great importance for most organic analyses. To demonstrate these changes in potential with pH, it is best to study quinhydrone. Practically no current flows at the midpoint of the polarographic wave of quinhydrone because this compound dissociates into equal parts of hydroquinone (reductant) and quinone (oxidant). This will become clear from the following experiment.

Experiment 2.—(*a*) Electrolyze, open to air, one cc. 0.02 *M* quinhydrone plus 9 cc. 0.1 *M* nitric acid between +0.45 and −0.30 volt using a saturated calomel half-cell as reference electrode and a potassium nitrate bridge as liquid junction. (*b*) Repeat the same procedure substituting 9 cc. of a McIlvaine buffer of pH 8 for the nitric acid. Here it is necessary to remove any dissolved oxygen by bubbling nitrogen through the solution so that the quinone diffusion current can be measured. Also some reaction between the quinone and oxygen will take place unless the buffer is freed of oxygen before the addition of the quinhydrone. Position No. 4 of the galvanometer shunt is suitable for these experiments. Determine the resistance of the circuit as described before[2, 5] and note the temperature.

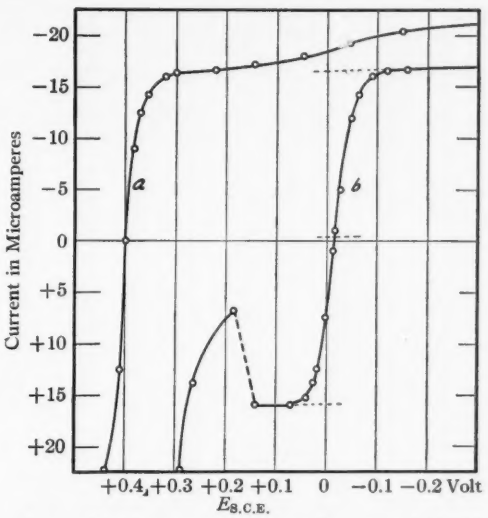

FIGURE 7.—CURRENT–POTENTIAL CURVES OF 0.002 *M* QUINHYDRONE IN (*a*) 0.1 *N* NITRIC ACID AND (*b*) MCILVAINE BUFFER OF pH 8

Figure 7 shows the two current–potential curves obtained in this fashion. The anodic diffusion current of the hydroquinone oxidation at pH 1 cannot be measured because the anodic dissolution of mercury interferes. However, the cathodic portion of this curve can be measured despite the presence of oxygen. A good curve is obtained at pH 8; it shows the same discontinuity of the anodic current that has been described in the preceding paper,[2] which might be called anodic passivity. These experiments were carried out at 24°C. so that we should expect a change of 0.059 volt per pH unit. At zero pH, the E'_0 for quinhydrone referred to the saturated calomel electrode is +0.453 volt. For pH 1 we would therefore calculate an E'_0 of +0.394 volt and for pH 8, −0.019 volt. The half-wave potential at pH 8, as indicated, is $E_{S.C.E.} = -0.015$ volt; that for pH 1, assuming that the anodic wave would have the same height as that in curve *b*, is +0.395. These half-wave potentials may be slightly in error due to differences in the diffusion coefficients of quinone and hydroquinone but, as may be seen from Figure 7*b*, the half-wave potential is practically identical with the potential observed when no current flows. Thus it is in good agreement with the results obtained in the potentiometric method, using a platinum electrode under the same conditions. Considering the experimental error involved in these measurements, it is therefore quite satisfactory to use the dropping mercury electrode as an indicator electrode in the presence of sufficient quinhydrone for potentiometric pH measurements. The following experiment will demonstrate this.

[10] *Chem. Rev.*, **24**, 95 (1939).

Experiment 3.—Add a few crystals of quinhydrone to 10 cc. each of 0.1 *N* nitric acid and McIlvaine buffers of pH 2, 3, 4, 5, 6, 7, and 8. The last of these should be analyzed immediately after the addition of quinhydrone. Note the temperature and measure the potential of the dropping mercury electrode in each solution against that of the saturated calomel half-cell, using a saturated potassium nitrate agar bridge. This is done by adjusting the potentiometer until the galvanometer is not deflected in either direction. Note that the oscillations of the galvanometer are almost completely abolished during the formation of the drops, showing the excellent poising action of these systems

The resulting potentials and the corresponding theoretical values are as follows:

pH	1	2	3	4	5	6	7	8
Observed potential $E_{S.C.E.}$	394	330	282	220	156	99	42	−22 millivolts
Theoretical potential $E_{S.C.E.}$	394	335	276	217	158	99	40	−19 millivolts

The agreement is as good as the accuracy of our apparatus permits. From this it becomes obvious that the dropping mercury electrode can also be used for some acid-base titrations (see Part I[4]). The advantages and disadvantages of this application cannot be discussed here.

The above pH–potential relationship could also have been demonstrated using the half-wave potentials of the reduction of a pure solution of quinone or the half-wave potentials of the oxidation of hydroquinone, since we have seen that they are all identical.[2] Solutions of the pure oxidant or reductant of any other reversible system could be studied in the same way. This feature is a distinct advantage of the polarographic method because all other reversible oxidation-reduction systems are available only in either fully oxidized or reduced form, necessitating titrations at each pH for the determination of E'_0. Unfortunately, the accuracy of the polarographic potentials is inferior so that the method can only be used for approximations.

Many of the irreversible reductions have been used in investigations of a theoretical nature. These include the effect of substitution in an organic molecule upon its reduction potential (ketones and aldehydes), reaction kinetics (inversion of sucrose, Cannizzaro reaction, molecular rearrangements), polymerization (formaldehyde, pyruvic acid), and tautomerism (keto-enol tautomerism, etc.). It is not possible here to discuss these at length.

Practical application of polarography in the vitamin field does not seem far off, since studies in pure solution have shown good curves for vitamins C and K and for some of the B complex. An outstanding recent practical application deserves special mention since it shows the most promising approach to the analysis of organic compounds. It is the polarographic determination of sex hormones in urine.[11] As might be expected, the hormones with an α,β-unsaturated ketone were found reducible, while those with a saturated carbonyl group were not. However, the latter could be condensed with excess Girard's reagent and thus be made suitable for polarographic analysis. The method was further extended to the determination of polarographically inert non-ketonic alcohols of the sterol group by oxidation of these substances to the corresponding ketones with aluminum *t*-butoxide and further treatment with Girard's reagent.

Special Applications. There are also some types of polarographic analyses in which the substance analyzed has only an indirect influence upon the current. Two of these will be mentioned here as examples.

The first depends on the suppression of the oxygen maximum (Figure 2, Part III[1]) which is considered a function of the surface activity of certain compounds. For comparison, that concentration of such substances is taken which is necessary to reduce to one-half the oxygen maximum obtained in dilute solutions. These analyses have been extended to studies of dyestuffs and oils. Also, in the analysis of drinking water, such observations have been helpful because the presence of impurities and bacteria will lower the otherwise prominent oxygen maximum.

The second analysis, which has received wide attention in recent years because of its possible clinical value, is a catalytic reaction at the dropping mercury electrode developed by Brdička.[12] As has been shown in Part III, Figure 4,[1] a sharp maximum is obtained in the reduction of cobalt ions. When Brdička attempted to suppress this maximum by the addition of protein to the solution, he succeeded, but also obtained an unexpected double-wave which did not appear in the same protein solution when cobalt was absent. Further investigations led Brdička to the conclusion that these waves are due to the reduction of hydrogen from sulfhydryl groups of the protein molecule, catalyzed by the presence of cobalt. He found, moreover, that this protein double-wave was smaller in the serum of patients suffering from cancer or various infectious diseases than in that of normal individuals. Studies are in progress in many laboratories to apply this observation as an aid to clinical diagnosis. So far it has been impossible to differentiate between specific diseases, such as cancer, pneumonia, and arthritis, although several modifications of the test have been devised. A correlation of polarographic data with observations made in electrophoresis experiments[4] should be of interest. The differences between normal and abnormal individuals are magnified if the proteins are partially denatured. Our simple apparatus[5] can be used for such analyses, as is demonstrated by the following experiment.

Experiment 4.—Add one cc. of water and 0.25 cc. of 1 *N* potassium hydroxide to one cc. of a 5 per cent solution of albumin. After 30 minutes, add 0.05 cc. of the digest to 10 cc. of cobalt buffer (4×10^{-3} *M* cobaltous chloride in 0.1 *N* ammonium chloride and 0.1 *N* ammonium hydroxide). Electrolyze this solution, open to air, between 0.8 and 1.9 volts using the galvanometer shunt at position No. 4.

The results are shown in Figure 8. The first wave

[11] WOLFE, HERSHBERG, AND FIESER, *J. Biol. Chem.*, **136**, 653 (1940); HERSHBERG, WOLFE, AND FIESER, *J. Am. Chem. Soc.*, **62**, 3516 (1940).

[12] *Collection Czechoslov. Chem. Commun.*, **5**, 112, 148, 238 (1933); *Acta Intern. Verein. Krebsbekämpfung*, **3**, 13 (1938).

represents the reduction of cobaltous ions and the following double-wave is due to the protein. The latter may assume various shapes depending on the concentration of protein and the temperature at which the experiment is performed. Its relation to the concentration of protein is not linear.

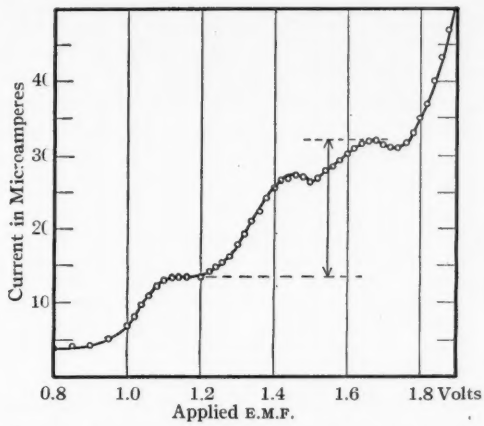

FIGURE 8.—CURRENT–VOLTAGE CURVE OF DENATURED ALBUMIN IN COBALT BUFFER

POLAROMETRY

Studies in which current–voltage curves are obtained manually suggest that whenever a plateau is reached, a constant applied voltage could be used for the determination of the substance. Before this idea could be put into practice complete polarographic investigations were needed to establish the necessary fundamentals. In Part III,[1] Experiment 6, is given an example of such an analysis; a linear relationship was found between concentration and observed diffusion current. In making this simplified application one must be sure (*a*) that the diffusion current is corrected for the residual current and any other current caused by the preceding discharge of another ion, and (*b*) that no significant error is produced by small variations in the applied voltage or by changes in the electrode potential due to changes in current. Since the applied voltage is kept constant and the current I is changing, the factor IR is likewise affected and will cause a change in the electrode potential.[2] One should therefore choose for such measurements an applied voltage at which a level plateau in the polarographic curve indicates that small changes in the applied voltage produce no measurable change in the resulting current. This principle was first applied by Müller and Baumberger[13] to the analysis of oxygen in solution. As may be seen from Figure 2, Part III,[1] after a maximum suppressor has been added, a satisfactory plateau permits such analyses in this solution over the range of -0.5 to -0.8 volt. For most buffered solutions an applied voltage of $E_{S.C.E.}$ -0.5 volt gives the best results. Baumberger[14] has applied this type of analysis to the study of oxygen consumption of yeast cell suspensions. This very convenient analysis may be demonstrated by the following experiment.

Experiment 5.—(*a*) To 10 cc. Sørensen's phosphate buffer of pH 6.9 add 0.5 cc. of a 10 per cent suspension of baker's yeast. After shaking the solution with air, observe the change in current with time at a constant applied voltage of -0.5 volt. Repeat this procedure several times after intermediate equilibration of the solution with air by vigorous shaking. (*b*) Add 0.5 cc. of 10 per cent glucose to the suspension and again observe the change of current with time.

This experiment was carried out with a Nejedlý polarograph (Figure 9) to show the simplicity with which such a current–time curve at constant voltage can be obtained. Notice the marked increase in the slope of the curve which represents an increase in respiration produced by the addition of substrate to the suspension.

A similar analysis may be carried out by observing the disappearance of oxygen from a solution upon the addition of sodium sulfite.

Experiment 6.—(*a*) At a constant applied voltage of -0.5 volt, observe the current after one cc. of 0.1 *M* sodium sulfite solution has been added to 20 cc. of 1 *N* potassium nitrate. (*b*) Repeat this experiment with a fresh solution of potassium nitrate to which has been added 0.5 cc. of a 2 per cent solution of gelatin. Observe the current for 10 minutes and add an additional one cc. of sulfite to the solution.

This experiment shows that if no gelatin is present in the solution, the reaction between sulfite and oxygen is so fast that it cannot be followed polarographically. When gelatin is present, however, the reaction rate is markedly decreased and is still measurable if twice the concentration of sulfite is present. This is an example of negative catalysis which can be conveniently studied with a polarograph.

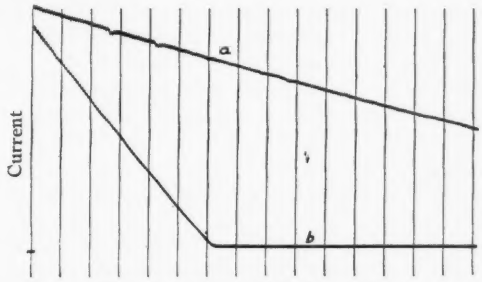

FIGURE 9.—POLAROGRAPHIC RECORD OF CURRENT–TIME CURVES REPRESENTING RATES OF OXYGEN CONSUMPTION OF YEAST CELLS
(*a*) In the absence of substrate
(*b*) In the presence of glucose

In this connection should be mentioned the so-called *increment method* in which the currents at two different applied voltages (theoretically at the beginning and end of the polarographic wave) are measured. The difference in current is here considered proportional to the concentration of the electro-active substance

[13] Paper presented before the December meeting of the Western Society of Naturalists (1935).
[14] *Cold Spring Harbor Symposia Quant. Biol.*, **7**, 195 (1939).

analyzed. This method must be used with caution, since no correction for residual current is made and since many ions may interfere if the two chosen voltages are far apart.

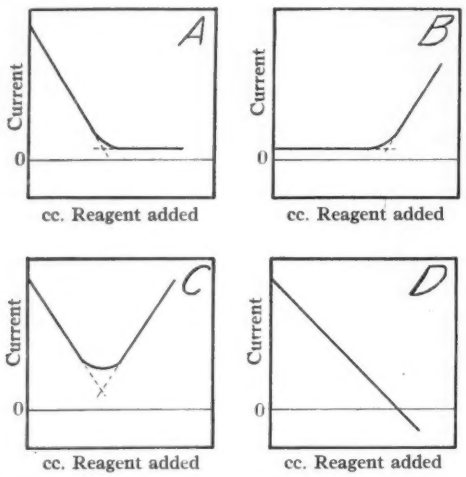

FIGURE 10.—TYPES OF POLAROMETRIC TITRATION CURVES

Besides the above relatively slow reactions, we have to consider the removal of electro-active substances by means of titration, which for successful application must be a very fast reaction. "Polarographic titrations" in which a complete polarogram was prepared after each addition of reagent were described by Heyrovský[15] as early as 1927. They involve considerable labor and have never become popular. In 1936, Majer[16] discussed such titrations theoretically and suggested the use of a constant applied voltage. He pointed out that precipitation reactions, oxidation-reduction titrations, and neutralization titrations should all be possible by this type of application. These he called *polarometric titrations* to show the relationship to the polarographic method. As an example, Majer published the polarometric titration of lead with sulfate ions and that of sulfate with barium ions. In the first case, the electrode is polarized sufficiently to reduce the lead ions; a large current is observed at the start of the titration which decreases to a finite limiting value as all the lead is precipitated. If the current is plotted against the quantity of reagent added, a curve of the type shown in Figure 10*A* is obtained. In the titration of sulfate with barium ions, the current is small at the outset and increases suddenly when an excess of barium is added (Figure 10*B*). Neuberger[7] described polarometric titrations in which organic precipitants were used, *e. g.*, the titration of nickel ions with dimethylglyoxime, that of copper ions with salicylaldoxime. He also showed a titration of lead with dichromate ions in which both the added reagent and the ion being titrated are reducible at the same applied voltage. This type of titration will produce a V-shaped curve with a very sharp break at the equivalence point (Figure 10*C*). Kolthoff *et al.*[17] have added to these studies and have confirmed the above titrations by more accurate analyses. They coined a new word for these reactions by calling them "amperometric" titrations. A fourth type of polarometric titration curve (Figure 10*D*) was first demonstrated by Strubl[18] in the oxidative-reductive titration of titanium. In this titration the current changes from anodic to cathodic or vice versa and the end of the titration is indicated by zero current. A similar curve is obtained in the titration of chloride, as suggested by Kolthoff and Lingane.[19] This is demonstrated by the following experiment.

Experiment 7.—Add 5 cc. of 1 *N* nitric acid to 10 cc. of 0.01 *N* sodium chloride. Titrate this solution by adding 0.01 *N* silver nitrate in aliquots of one cc. Observe the current during this titration, applying +0.3 volt to the dropping mercury electrode. Use the saturated calomel half-cell as cathode and an agar bridge saturated with chloride-free potassium nitrate as liquid junction. (The nitric acid is necessary to bring about a sufficiently rapid precipitation.)

The corresponding titration curve is represented in Figure 11. It shows that if the titer of the silver nitrate solution was accurate, the sodium chloride must have been 0.0102 *N*. It also demonstrates the simplicity with which such titrations can be carried out. The

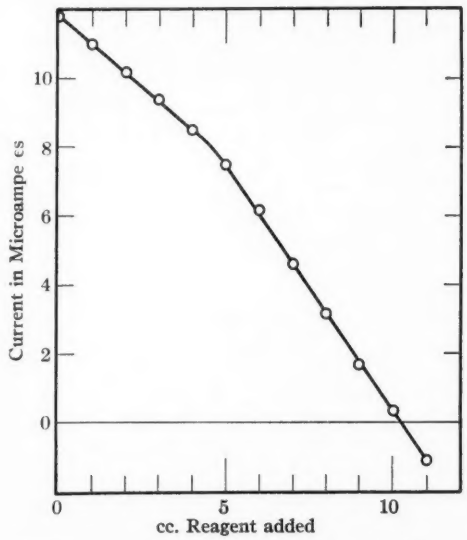

FIGURE 11.—POLAROMETRIC TITRATION OF SODIUM CHLORIDE WITH SILVER NITRATE

volume additions can be made of a convenient size and need not be modified near the equivalence point, which is usually obtained by the extrapolation of straight lines.

[15] *Bull. Soc. chim. France*, **41**, 1224 (1927).
[16] *Z. Elektrochem.*, **42**, 120, 123 (1936).
[17] KOLTHOFF AND PAN, *J. Am. Chem. Soc.*, **61**, 3402 (1939) and **62**, 3332 (1940); KOLTHOFF AND LANGER, *J. Am. Chem. Soc.*, **62**, 211, 3172 (1940).
[18] *Collection Czechoslov. Chem. Commun.*, **10**, 475 (1938).
[19] *Chem. Rev.*, **24**, 1 (1939).

As is evident, the curves obtained in polarometric titrations resemble the conductometric titration curves shown in Part I.[4] They are, unfortunately, subject to the same shortcomings. The precipitation must be rapid and should not form unwanted complexes; the precipitate must not remove any of the electro-active material by adsorption; the solution should not become so viscous or filled with flocculent precipitate that the dropping becomes irregular or that diffusion rates are changed. For best results the titrating agent should be fairly concentrated so that the volume change will be negligible. If necessary, corrections for volume change can be made by multiplying the observed current I by a factor, $(V_0 + V_a)/V_0$.[18] In this way a straight line can be obtained which permits extrapolation to the endpoint.

Polarometry seems most promising for industrial applications since the equipment and technic necessary are most simple. However, much work needs to be done before it is possible to apply polarometry to every unknown.

ACKNOWLEDGMENT

It is a pleasure to acknowledge my indebtedness to the late W. E. Benjamin, whose generous gift of funds to Dr. John Staige Davis, Jr., has made the publication of these articles possible. I am also indebted to Mr. Donald M. Phillips for assistance in some of the experiments.

The Pallid Veil

THE atmosphere near the earth's surface, even when not fouled by man, is full of microscopic particles—mainly salt crystals near the sea, more often the results of abrasion and combustion farther inland. Over industrial areas, droplets of sulfurous acid are prominent, estimates being made that, on a winter day, the city of New York vents into the air above it some 2000 tons of sulfur dioxide. In sections of heavy pollution, from several hundred to many thousand tons of sulfur compounds, carbon particles, and assorted dusts may settle on each square mile in the course of a year.

Many of these solid and liquid specks are hygroscopic and form excellent nuclei for water droplets when the temperature of the atmosphere falls to the dew point. Although fog would form with considerable difficulty in an atmosphere entirely free of nuclei, hygroscopic particles are always so common in nature that the frog droplets utilize but a small fraction of those available. Fog droplets are small, generally under 0.002 inch in diameter, but the nuclei are so much smaller that they constitute scarcely one part by weight in 10,000 of fog. To produce the conditions of limited visibility and clammy feeling known as fog, a cubic meter of air need not contain more than 0.1 to 0.4 gram of water as fog droplets. Visibility, in fact, is a means of defining fog, that phenomenon being usually regarded as a cloud which envelops the observer and which reduces the horizontal visibility to 1000 meters or less. In city fogs, whose droplets are generally smaller than those of sea fogs, visibility may be considerably less for the same water content. Much of the basic knowledge on the properties of fog was not available until quite recently.

Natural fog has many structural counterparts in industry, common types being the oil fogs sometimes seen in automobile exhausts and the tar fogs that form in coal gas and coke oven gas as they drop in temperature after leaving the retorts. Here an envelope of oil or tar forms about carbon nuclei. Probably the best known type of industrial fog is the stable and destructive mist obtained when waste gases carry sulfur dioxide, sulfur trioxide, or sulfuric acid into the atmosphere. Among methods used to combat it are electrical precipitation and a recently announced absorption process in which the mist is bubbled through water containing special foaming agents, the most effective being the "green acid" obtained from the sludges of oil-refining plants. A very fine spray of new design has recently been found effective in absorbing chemical fogs which are passed through a special cyclone scrubber.

As may be gathered from the ease with which it will tie up traffic, slow ships to a crawl, ground airplanes, and hurry already weakened individuals into eternity, even stronger incentives exist to reduce natural fog. The remarkable fog that covered the valley of the Meuse in Belgium from December 1 to 5, 1930, was accompanied by thousands of cases of respiratory troubles, over 60 human deaths on the third and fourth day, and many fatalities among cattle and small animals. Other evidence exists that the frequency of pulmonary and cardiac failures increases in industrial areas in periods of heavy fog. To a world port, furthermore, the cost of transportation delays is measured by the millions of dollars. At LaGuardia Field, New York City, for example, a fog in late December, 1940, forced the cancellation of 617 airplane flights in a period of two days.

Attempts to improve visibility by artificial illumination are stymied by the thoroughness with which the myriads of tiny fog particles, up to 100 per cubic centimeter, scatter light. The action is as effective at one visible wave length as at another; even infra-red radiation does not give a practical degree of improvement in penetration, the wave lengths in the near infra-red region being still too short for effective penetration, while those in the far infra-red region are absorbed to a great extent by the water vapor and carbon dioxide always present in the atmosphere. The numerous investigations on the action of light rays in fog (most of them concerned with the effectiveness, if any, of colored

automobile lights in foggy weather) overwhelmingly conclude that, if a colored beam shows any improvement in visibility over one of equal intensity from an unfiltered incandescent light, the effect is purely psychological.

Attempts to improve visibility by bodily removing the fog, while quite feasible scientifically by a number of ways, have so far been limited in practice by the enormous dimensions of the problem. In a volume 1500 feet long, 130 feet wide, and 30 feet high there may be present as fog droplets from 150 to 700 pounds of water, an amount which must be removed over and over again since fogs, while ordinarily slow moving, still have velocities up to about fifteen miles per hour.

While fogs can be destroyed by electrical precipitation and by supersonic vibrations, the most promising methods appear to be those which lower the relative humidity of the air sufficiently to cause rapid evaporation of the fog droplets. Houghton and Radford of the Massachusetts Institute of Technology have used sprays of concentrated solutions of drying agents like calcium chloride. With the latter salt, they have kept a volume about 1800 feet long, 130 feet wide, and from 30 to 60 feet high free from fog by the expenditure of 85 gallons of saturated solution per minute. The fogs cleared away had speeds up to sixteen miles per hour. The cost of drying agent used, assuming a nearby source of calcium chloride solution, would be about $220 per hour. Equipment such as this, with perhaps somewhat larger capacity, might be used to clear the dangerous last hundred feet of descent for a fog-blinded airplane landing by use of instruments.

Houghton and Radford estimate that to keep the same volume clear by the use of heat would require the expenditure of about 5000 kilowatts continuously. The difficulty would be not in supplying the necessary energy, but in releasing or transmitting it evenly over such a volume.

—Reprinted from the "Industrial Bulletin" of Arthur D. Little, Inc., Number 167, March, 1941

A COMPACT CALOMEL ELECTRODE

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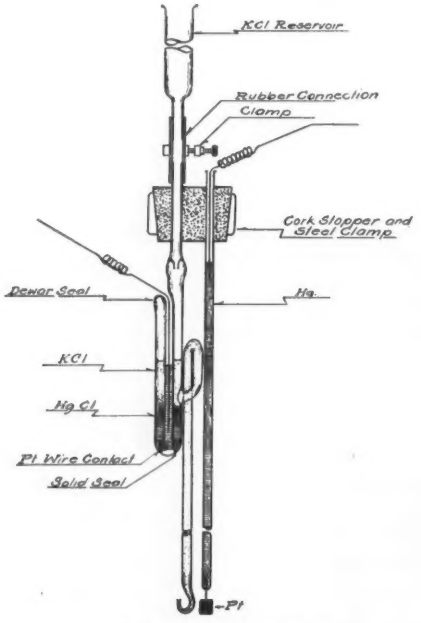
THE calomel electrode shown in the accompanying figure[1] has proved quite convenient for electrometric titrations with the quinhydrone electrode, especially in titrations at small volume. The vertical arrangement of the parts saves space in the titration assembly, which must include the two electrodes, a buret, and a stirrer. The addition of potassium chloride is controlled by a pinchclamp, the ring-sealed jet permitting observation of the rate of addition. Electrical contact with the calomel cell is made through the inner tube, the platinum wire being included in the solid seal at the bottom.



CALOMEL ELECTRODE

Since the apparatus includes a platinum seal, it should be made up in soft glass, but pyrex glass may be used if the platinum wire is beaten thin and a bead of pyrex glass is melted on it and pressed down firmly. This bead is then fused onto the flared inner tube before making the solid seal. The body of the cell may be made in any convenient dimensions, from 13 by 50 mm. to 22 by 125 mm. The delivery tube, which is pictured straight in the diagram, may be bent into any convenient position. A shorter platinum electrode may be mounted by means of a cork to the lower portion of the delivery tube, in which case the calomel cell may be protected in the intervals between use by a vial of potassium chloride.

Calomel electrodes of this design are not as easily broken as the conventional Hildebrand model, because there is only one projecting side tube, and this tube may be fastened to the body of the cell with cork and wire. Measurement of pH may be made with samples as small as one ml. and titrations are readily carried out on 50-ml. samples. In two years of service, this calomel electrode has proved very rugged, stable, and convenient.

[1] Drafting by courtesy of Professor H. E. Brookman.

Demonstrating the Movements of Colloidal Particles

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INTRODUCTION

IF A liquid containing very fine particles in suspension is examined under a microscope, the suspended matter will be found to be in a state of constant motion. Convincing evidence has been offered by Einstein and others which indicates that this phenomenon, known as Brownian movement, is due to the bombardment of the particles by the molecules of the liquid.

A second characteristic of a substance in colloidal suspension is the electrical charge which each particle carries. Whether the charge is positive or negative depends upon such factors as ion adsorption and the relationship between the dielectric constants of the substance in suspension and its carrier liquid.

While the primary movement of colloidal particles is the result of bombardment, the path which they follow is altered by the electrical charge they possess. Since bodies which carry a charge of the same sign repel one another, and since the particles of a given colloid usually carry charges of the same sign, a colloidal particle driven by molecular impact into the electrostatic field of a neighboring particle will not only tend to repel that particle but will itself suffer repulsion. All particles set in motion by this procedure encroach upon the domains of other particles, resulting in an endless repetition of the action described.

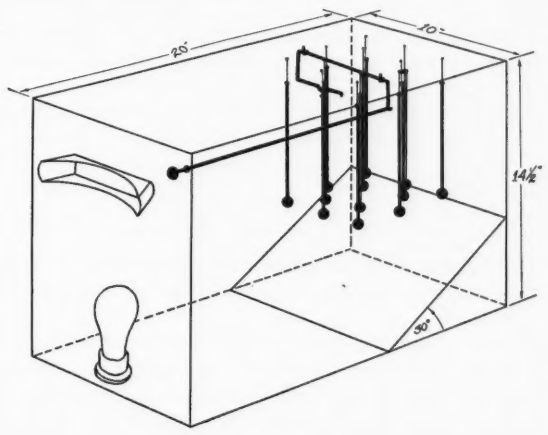

FIGURE 1

DEMONSTRATION DEVICE EASILY CONSTRUCTED

A simple device to demonstrate the movement of colloidal particles may be constructed from a dozen magnetized rods,[1] an equal number of small wooden balls,[2] a mirror, a little luminous paint, a 40-watt bulb, and a rectangular box to house the parts. These are assembled as illustrated in Figure 1.

The rods are 1/4 inch in diameter, approximately 6 inches long, and are made of steel stock that is capable

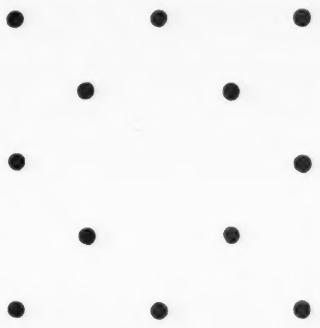

FIGURE 2

of being permanently magnetized. The rods, after magnetization, are suspended from the roof of the box in a pattern as indicated in Figure 2, and are so hung that the poles of like sign all point in the same direction. The lower end of each rod is fitted with a wooden ball having a diameter of approximately one inch. These balls are treated with luminous paint of the type used on clock and watch dials. It is important that the rods swing freely. This may be accomplished by fitting to the opposite end of the magnet a smaller wooden ball through which passes a short piece of black thread secured by a knot and fastened to a screw-eye in the ceiling of the box (see Figure 3).

FIGURE 3

In order to make the illusion of particle movement more complete, a mirror is placed immediately beneath the rods in such a manner as to form a 30° angle with the bottom of the box. It is also well to provide a simple illumination system consisting of a 40-watt bulb, which may be operated by a toggle switch mounted on the face of the box.

The box is also provided with a small opening through which the action may be

[1] It should be explained to the student that the *magnetic* forces involved in this model simulate the *electrostatic* forces involved in its colloidal analog.

[2] If lacquered wooden beads from novelty necklaces are used, remove the lacquer with acetone before applying the luminous paint.

viewed. This window is fitted with a shield constructed from the eyepiece of a stereoscope from which the lenses have been removed. To eliminate reflection, the entire interior of the box as well as the rods, with the exception of the phosphorescent balls, is painted a flat black. A "starter bar" comprised of a rod extending through the front of the instrument and designed to contact a single suspended magnet completes the device.

METHOD OF OPERATION

In employing this device, first illuminate the interior in order that its construction may be studied. This step serves a double purpose inasmuch as it also activates the luminous paint covering the balls. Phosphorescent preparations usually lose their brilliance unless exposed to strong light from time to time.

The next step is to extinguish the light and, with the aid of the starter bar, to set one rod in motion—an act which may be regarded as simulating molecular impact. This rod, by cutting into the electromagnetic fields of its neighbors, eventually causes all of the rods to oscillate in a haphazard manner.

Upon peering into the darkened box, one finds that only the balls are visible. These, together with their reflections in the mirror, represent particles in suspension; and their movements realistically mimic the Brownian movement of colloidal particles.

This demonstration has been found commercially useful by this company's sales engineers in making more understandable to laymen the reasons why colloidal graphite suspensions are stable, and seemingly defy the law of gravity. Although individuals were frequently given an opportunity to view Brownian movement and particle repulsion under a microscope, it was not until the present instrument was designed that they clearly understood the principles involved.

It is quite possible that a working model of this type, originally built as a sales aid, will be found even more useful in the classroom.

Use of Cobaltous Sulfate in Qualitative Organic Analysis

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INTRODUCTION

IN THE study of qualitative organic analysis considerable emphasis is usually placed on the relationship of molecular structure to solubility. A number of writers have used solubility as a means of classifying organic compounds. For this purpose water, dilute alkalies, dilute acids, and cold concentrated sulfuric acid are usually recommended as solvents. In the procedure followed in the text by Shriner and Fuson[1] water-soluble compounds are subdivided according to their solubility in ether; acidic compounds, soluble in sodium hydroxide, according to their solubility in sodium bicarbonate; and neutral compounds, soluble in cold concentrated sulfuric acid, according to their solubility in phosphoric acid. No subdivision is made of the basic compounds soluble in hydrochloric acid. It is the purpose of this paper to describe a reagent that can be used to classify further such organic bases.

In order to make the proposed subdivision a precipitation reaction, rather than a solubility test, is employed. The reagent used, cobaltous sulfate, dissolves in water to give a red colored solution with a pH value of approximately 4.6 for a five per cent solution.[2] If the solution of the salt can be made sufficiently basic, blue cobaltous hydroxide[3] will precipitate. Britton[4] has shown that the precipitation of the hydroxide will start at a pH of 6.81. Aliphatic amines and certain aromatic amines, like benzylamine, are sufficiently strong as bases to bring about the precipitation of cobaltous hydroxide. Weaker bases, of the order of aniline, although soluble in hydrochloric acid, will not precipitate the hydroxide. Cobaltous sulfate therefore can be used to distinguish between these two types of organic bases.

DIRECTIONS FOR TEST

The amounts of materials used are the same as those suggested for solubility tests in the text by Shriner and Fuson.[1]

Place 0.2 ml. (0.1 g. of a solid) of the sample in a test tube and add 3 ml. of five per cent cobaltous sulfate. Shake the tube and note the formation or non-formation of blue cobaltous hydroxide. If a precipitate does not immediately form set the test tube aside; if the precipi-

[1] SHRINER AND FUSON, "Identification of organic compounds," 2nd ed., John Wiley and Sons, Inc., New York City, 1940, p. 4.

[2] DENHAM, "The electrometric determination of the hydrolysis of salts," *J. Chem. Soc.*, **93**, 61 (1908).

[3] Interesting discussions on the formation of cobaltous hydroxide may be found in the following references:
STILLWELL, "The colors of cobaltous hydroxide," *J. Phys. Chem.*, **33**, 1247–72 (1929).
WEISER AND MILLIGAN, "The transformation from blue to rose cobaltous hydroxide," *J. Phys. Chem.*, **36**, 722–34 (1932).

[4] BRITTON, "Electrometric studies of the precipitation of hydroxides," *J. Chem. Soc.*, **127**, 2110 (1925).

tate does not form within five minutes the test is considered negative.

The results obtained with a number of compounds are shown in Table 1. Dissociation constants are included, in the form of pK values, in order to show the approximate dividing line between a positive and a negative test. α-Picoline, pK 7.5, does not give an immediate test but is positive in reaction within five minutes. A practical dividing line then may be set at a pK value of approximately 7.5.

TABLE 1
AMINES TESTED

Compound	*pK*	*Formation of Precipitate**	*Color of Precipitate*
Piperidine	2.9	+	Blue
Triethylamine	3.2	+	Blue
Di-*n*-butylamine	3.3†	+	Blue
Ethanolamine	3.3†	+	Blue
Benzylamine	4.6	+	Blue
2,4,6-Collidine	6.7	+	Blue
α-Picoline	7.5	±	Blue
Methylaniline	8.1	−	
Pyridine	8.6	−	
p-Toluidine	8.7	−	
Quinoline	9.2	−	
Aniline	9.3	−	
m-Toluidine	9.3	−	
o-Toluidine	9.5	−	
o-Phenylenediamine	9.5	−	
Dimethylaniline	9.6	−	
β-Naphthylamine	9.7	−	
α-Naphthylamine	10.0	−	

* Immediate precipitation +; precipitation within five minutes ±: no precipitation −.
† Estimated.

The reagent may be used to advantage with water-soluble bases. Table 1 lists a number of such substances. With water-soluble compounds a negative test would, of course, indicate only the absence of a base capable of precipitating cobaltous hydroxide and not necessarily the presence of a compound of the pyridine order of basicity.

EFFECT OF IMPURITIES

A study was made to determine the effect of certain impurities on the test. The presence of any base capable of precipitating cobaltous hydroxide, such as ammonium hydroxide or sodium hydroxide, may of course produce confusing results. A number of substances tested for interference with benzylamine and ethanolamine are listed in Table 2. In each case both the amine and the impurity were varied simultaneously in order to maintain a constant sample value of 0.2 ml (0.1 g. of solid). The results listed in the table are entirely qualitative in nature and are not intended to fix interference limits. Rather, they serve mainly to point out the facts that in the presence of certain reagents the precipitated hydroxide is not always blue in color and occasionally precipitation may even be prevented (note effect of sodium citrate).

TABLE 2
EFFECT OF IMPURITIES*

Compound	*Amount of Impurity*	*Amount of Amine*	*Color of Precipitate* Benzylamine	Ethanolamine
Ethylene glycol	0.05 ml.	0.15 ml.	Blue	Blue
Ethylene glycol	0.10 ml.	0.10 ml.	Blue	Blue
Ethylene glycol	0.15 ml.	0.05 ml.	Blue	Blue
Glycerol	0.05 ml.	0.15 ml.	Blue	Blue
Glycerol	0.10 ml.	0.10 ml.	Blue	Blue
Glycerol	0.15 ml.	0.05 ml.	Blue	Blue
Dextrose	0.025 g.	0.15 ml.	Blue	Blue
Dextrose	0.05 g.	0.10 ml.	Blue	Blue
Dextrose	0.075 g.	0.05 ml.	Blue	Blue
Dimethylglyoxime†	0.025 g.	0.15 ml.	Green	Green
o-Phenylenediamine	0.025 g.	0.15 ml.	Blue	Blue
o-Phenylenediamine	0.05 g.	0.10 ml.	Blue	Blue
o-Phenylenediamine	0.075 g.	0.05 ml.	Blue	Blue
Sodium citrate	0.025 g.	0.15 ml.	Blue	Blue
Sodium citrate	0.05 g.	0.10 ml.	Blue	Blue
Sodium citrate	0.075 g.	0.05 ml.	No precipitate	No precipitate
Sodium tartrate	0.025 g.	0.15 ml.	Blue	Blue
Sodium tartrate	0.05 g.	0.10 ml.	Pink	Purple
Sodium tartrate	0.075 g.	0.05 ml.	Pink	Pink

* In each test 3 ml. of 5% $CoSO_4$ were used.
† No suitable conclusions could be reached with higher concentrations of dimethylglyoxime.

SPOT TESTS

A variation of the general test may be employed to obtain spot tests. Three drops of a two per cent cobaltous sulfate solution are placed on a spot plate. The addition of one drop (or a few milligrams of a solid) of an appropriate base will produce the precipitate of cobaltous hydroxide. Occasionally, as is the case with ethanolamine, the blue precipitate may change in color within a few seconds to a pink or red (presumably the more stable modification of cobaltous hydroxide). With the spot test technic α-picoline gives a faint blue precipitate within two minutes; a more noticeable precipitate is obtained in three to five minutes. All the other compounds listed in Table 1 as positive in reaction give an immediate blue precipitation in the spot test.

PITTSBURGH—CALIFORNIA EXCHANGE

DR. ALEXANDER LOWY, Professor of Organic Chemistry in the University of Pittsburgh, a graduate of Columbia University, has been invited to take charge of organic chemistry courses in the University of Southern California, Los Angeles, during the summer of 1941 in exchange with Dr. LeRoy S. Weatherby, Professor of Organic Chemistry in Southern California, who is a graduate of the Universities of Kansas and Chicago. The exchange professors will not only look after the full-year undergraduate courses which both institutions give during the summer, but also graduate courses and the direction of research in organic chemistry.

Selling a Chemistry Course to Factory Workers

CLAUDE H. SPIERS *Leathersellers Technical College, London, England*

ANYONE who has had to teach essentially practical subjects to factory workers taking evening classes is painfully aware of their reluctance to learn the theoretical side of a subject. It is true that these students come to night classes to advance their knowledge and skill, but because they work mainly with their hands and only to a limited extent with their minds, they have formed a very firm opinion that courses should consist mainly of work with the hands with a minimum of formal verbal instruction such as lectures. Moreover, the verbal instruction most readily acceptable is that describing the practical work rather than a theoretical explanation of it. Yet a basis of pure theory is usually essential.

The writer has had experience of this "sales resistance" to theoretical instruction in attempting to teach a little fundamental elementary chemistry and physics to tannery workers coming to college to study leather manufacture. The students tend to be frightened away from even attempting to attend science classes whose syllabus is described along conventional lines. The syllabus of a First-Year Leather Trades Science Class was formerly described in terms such as the following.

LECTURES

Elementary Chemistry and Physics. Measurement of length, area, and volume. Specific gravity, measurement by hydrometer, importance in control work. Evaporation. Leather drying. Solubility. Diffusion. Colloidal solutions. Chemical and physical change. Elements and compounds. Formulas and equations. Tannery calculations. Chemistry of chief compounds used in leather manufacture. Main types of chemical changes occurring in leather manufacture.

Principles of Qualitative and Quantitative Analysis. Applications of analysis to the examination of beamhouse and tannery materials.

PRACTICAL WORK

Simple experiments illustrating the nature of chemical and physical change.

Study of the properties and reactions of some of the main substances used in leather manufacture.

Elementary qualitative analysis. Detection of impurities and adulterants in tannery chemicals, leather, etc.

Determination of specific gravity by the specific gravity bottle, the barkometer, Baumé and Twaddell hydrometers.

Simple gravimetric and volumetric analysis. Determination of moisture, ash, total solids, water-soluble matter, grease, etc., in hides, leather, etc. Preparation of standard solutions of acids and alkalies. Estimation of the strengths of various acids, alkalies, sodium sulfide, etc.

Although throughout the lectures the practical needs of the students in their everyday work were kept in view, the syllabus proved somewhat unsuccessful in attracting many pupils. The topics did not suggest much connection with what was done in the factory.

The problem of writing out a syllabus with more drawing power was then tackled. The former syllabus had been developed by considering what theoretical topics should be understood in order to comprehend leather manufacture and to control it. In describing the scope of the course, the theoretical topics are mentioned and emphasized; it is not made clear what immediate help the student will receive in the performance of his everyday work. A new approach was therefore made by considering what scientific contacts a worker makes in the course of his daily routine, what measurements he has to make, what chemicals he uses, what chemical processes he carries out, what physical processes he supervises, etc. Consideration was given to the sort of questions that an intelligent worker would ask about his work. Then a selection was made of the topics which would have to be dealt with, and these were arranged in order to form a course which would be useful, logically developed, and designed to give a proper background of theoretical knowledge. The new syllabus forming the first-year course was the following.

I. Measuring the thickness of leather. Slot gage, dial gage, micrometer screw gage, etc.
II. Measuring the area of leather. Planimeter, pinwheel measuring machine, etc.
III. Weighing out chemicals in the tannery.
IV. Measuring the volumes of pits, buckets, paddles, drums, etc., and the importance of these measurements.
V. Measuring and controlling temperatures in the tannery. Distance thermometers. Automatic temperature control.
VI. Making up solutions in the tannery. Expressing the strengths of solutions.
VII. Cutting value of sole leather and its density and porosity.
VIII. Judging the quality of materials from density measurements.
IX. Control of liquors by hydrometers, barkometers, etc.
X. How to look after leather drying. Automatic humidity control.
XI. Water costs money. Finding the water in skins, oils, leather, etc.
XII. What things are made of. Elements, compounds, mixtures, etc.
XIII. The burning of materials. Ashing leather, pelt, etc.
XIV. What are acids? Properties of tannery acids.
XV. Nature of alkalies. Properties of tannery alkalies.
XVI. Salts and how they are formed. Properties of tannery salts.
XVII. More about salts. Normal, acidic, and basic salts.
XVIII. Neutralization. Deliming and depickling of skins.
XIX. The rules that chemicals must obey. Atoms, molecules, formulas, and equations.
XX. Some useful tannery calculations.
XXI. Lime and chalk.
XXII. Pipets, burets, and titrations. Controlling soaking and pickling.
XXIII. How and why water supplies vary.
XXIV. Making water right for tanners.

Each class is complete in itself and is devoted to one topic. The above titles describe both the lectures and

the practical work; these are related to each other. It will be observed that the field covered is essentially the same as in the former case. But everywhere the practical aspects are emphasized. The various necessary theoretical topics are dealt with in the course, but most of them are not directly mentioned. The practical items imply a knowledge of the theoretical principles set out in the former syllabus. It is clear from the syllabus that each class deals with a point of practical importance to the worker in the tannery, explaining what he does and answering questions that must form in his mind. From every class, right from the beginning, something can be carried away to apply to practical work. At the same time the course is educational in the best sense because it teaches elementary chemistry and physics in a logical and systematic manner.

It can be asserted that the new syllabus has succeeded in attracting more students and holding their attention over a longer period so that they have been induced to attend in subsequent years for further instruction. "Packing and display" help in "selling" education just as in selling material commodities.

An Improved Dilatometer

ARTHUR FURST

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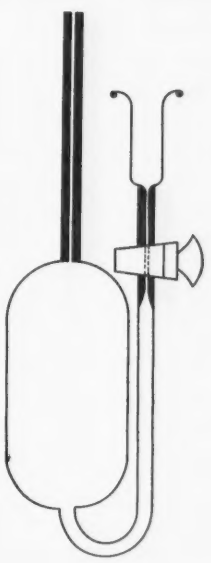
IT IS possible to follow reactions that are accompanied by a change in volume by means of a dilatometer. This instrument is essentially a bulb to which is sealed a capillary tube, and it is by the rise or fall of the liquid level in the tube that the volume change can be noted. To be efficient, a dilatometer must be filled easily in a relatively short space of time, and it must not introduce any extraneous errors; *e. g.*, an error in volume readings due to the drainage of the capillary tube. In dilatometry the solutions are mixed before being introduced into the dilatometer. The time of filling becomes of prime importance when a reaction goes to apparent completion in about two or three minutes. To obtain true rates of volume change it is best that the capillary tube be dry. If the bulb is filled by means of the capillary, the first few readings must be neglected. This is of importance only when an increase in volume is the net result.

A typical study of a physical-chemical reaction rate as outlined by Daniels, Mathews, and Williams[1] is the hydrolysis of acetal. The dilatometer described is constructed by sealing a capillary tube to a bulb, and then, in turn, sealing a tube of larger diameter to the capillary. The instrument can be filled by evacuating the system and allowing a previously mixed reaction mixture to flow in. During this procedure the reaction is taking place. The bottom bulb is filled by means of the connecting capillary tube. At times it is necessary to evacuate twice before the dilatometer is completely filled, since the capillary restricts the flow of incoming liquid. The excess liquid in the capillary tube is removed by a very fine capillary. Although the seals are so contructed that the error due to drainage is minimized, this source of error is still present; thus the first few readings must be neglected.

The drawbacks in using this type of dilatometer are: (1) method of filling; (2) time of filling; and (3) drainage error.

[1] DANIELS, MATHEWS, AND WILLIAMS "Experimental physical chemistry," 2nd ed., McGraw-Hill Book Co., Inc., New York City, 1934, p. 143.

In an attempt to overcome these disadvantages, a modified dilatometer was designed. (See figure.) The advantage of this type lies in the fact that the drainage error is eliminated by a method of filling from the bottom. A capillary stopcock is used in order to prevent air bubbles from remaining in the tube leading to the bulb. The stopcock can be shut before the level of the solution rises above the reference point in the capillary tube. The reservoir may be of larger capacity than the main bulb. This is especially desirable in the case of rapidly reacting solutions. Care must be taken that the level of the liquid in the reservoir above the stopcock does not get below the seal, for this will introduce air into the system. The dilatometer may be left in the thermostat during the process of filling.



The capillary tube can be graduated by pasting a strip of millimeter graph paper on it, the glass in front of the paper acting as a magnifier. A fine capillary (not shown) may be inserted in the capillary of the dilatometer to remove any liquid and to adjust the level to a convenient reference point.

For solutions that are reacting too rapidly the time of filling may be decreased by attaching the capillary to an aspirator, but if this is undesirable the reservoir can be filled, the stopcock opened, and pressure applied.

The suggested dilatometer was used for the study of the hydrolysis of acetal and excellent results were obtained.

The Valence Angle of the Carbon Atom

GORDON L. GOMBERT *Kent State University, Kent, Ohio*

IN EXPLAINING optical isomerism a model of the carbon atom, as in Figure 1, is practically essential. It is mentioned that the four atoms or groups united with the carbon atom are equally distant from each other because the angles between the carbon valences are equal. In such discussions the statement is usually made that this angle is 109°28′, but few organic texts, if any, offer a proof for this value, leaving this to the mathematical initiative of the student.

FIGURE 1

The tetrahedral conception of the carbon atom is attributed to van't Hoff (*1*) and Le Bel (*2*) who published papers on this geometrical spatial arrangement of atoms in 1874. It is possible that their ideas grew out of those already advanced by Wollaston (*3*) in 1808, Pasteur (*4*) in 1860, and Kekulé (*5*) in 1867. The tetrahedral carbon atom is today substantiated by X-ray investigation of the diamond by Bragg (*6*), and more recently by means of quantum mechanics by Pauling (*7*).

In solving this problem I found that a model, shown in Figure 2, of a regular tetrahedron with specially opening sides was particularly helpful. The model was prepared from four identical equilateral triangles, joined so as to form a regular tetrahedron, *V–ABC*. Then in order to study the center of the figure, where the valence angles are located, a vertical plane was passed through the vertex *V*, bisecting the base and one face in the lines *AM* and *VM*, respectively. At the same time one of the face triangles and half the bisected face were hinged along the base and allowed to open. The radii, *OA* and *OV*, were drawn from the center *O*, which is the point of intersection of the four altitudes of the tetrahedron, to the two vertices lying on the bisecting plane. The radius *OV* was continued to *F*. With these lines drawn, the value of the valence angle α may be calculated.

In triangle *ABM*

$$\overline{AB}^2 = \overline{AM}^2 + \overline{BM}^2$$

and letting each of the edges, that is *AB*, *AV*, *VC*, and *BC*, of the tetrahedron equal *S* and since

$$\overline{BM} = \frac{S}{2}$$

we have

$$S^2 = \overline{AM}^2 + \frac{S^2}{4}$$

which reduces to

$$\overline{AM} = \frac{S}{2}\sqrt{3}$$

Since *VF* is the altitude of the regular tetrahedron *V–ABC*, it meets the base triangle *ABC* at the point *F* which is two-thirds distant from the vertices of this triangle and one-third distant from the midpoints of its bases. Therefore

$$\overline{AF} = \frac{2}{3}\overline{AM}$$

or by substitution

$$\overline{AF} = \frac{S}{3}\sqrt{3}$$

and

$$\overline{FM} = \frac{1}{3}\overline{AM}$$

$$= \frac{S}{6}\sqrt{3}$$

In the triangle *VFA*

$$\overline{AV}^2 = \overline{VF}^2 + \overline{AF}^2$$

or

$$\overline{VF}^2 = S^2 - \frac{S^2}{3}$$

$$\overline{VF} = S\sqrt{\frac{2}{3}}$$

Also

$$\overline{OF} = \overline{VF} - r$$

$$= S\sqrt{\frac{2}{3}} - r$$

In triangle *AOF*

$$r^2 = \overline{OF}^2 + \overline{AF}^2$$

and substituting values of *r* and *S* for *OF* and *AF*

$$r^2 = \left(S\sqrt{\frac{2}{3}} - r\right)^2 + \left(\frac{S}{3}\sqrt{3}\right)^2$$

$$= \frac{2}{3}S^2 - 2rS\sqrt{\frac{2}{3}} + r^2 + \frac{S^2}{3}$$

$$S^2 = 2rS\sqrt{\frac{2}{3}}$$

$$S = 2r\sqrt{\frac{2}{3}}$$

Solving for r we get

$$r = \frac{S}{2\sqrt{\frac{2}{3}}}$$

Angle α equals

$$180° - \beta$$

or

$$180° - 70°31'36'' = 109°28'24''$$

In the preparation of this paper the author is grateful for the constructive criticism given by Professors E. M. Collins, M. B. Palmer, and F. L. Brooks of Kent State University.

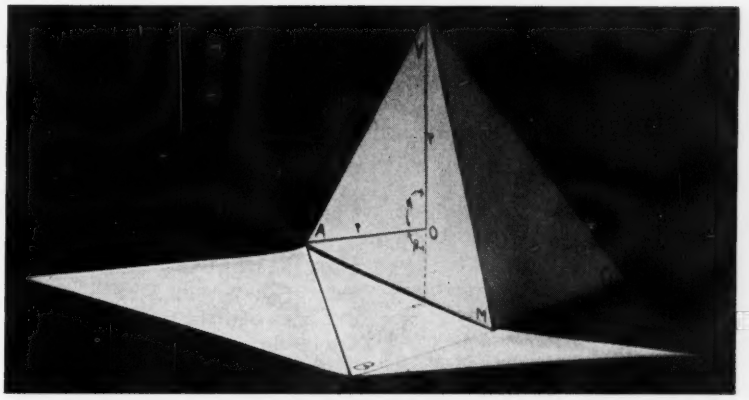


FIGURE 2

Also in this same triangle

$$\text{Sin } \beta = \frac{\overline{AF}}{r} = \frac{S}{3}\sqrt{3} \div \frac{S}{2\sqrt{\frac{2}{3}}}$$

Then by canceling the S's

$$\text{Sin } \beta = 0.94280$$

and

$$\beta = 70°31'36''$$

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INORGANIC CHEMICAL NOMENCLATURE

THE 1940 Report of the Committee of the International Union of Chemistry for the Reform of Inorganic Chemical Nomenclature, a summary of work done over a period of years, is probably the most important step taken in inorganic chemical nomenclature since the work done by Berzelius over a century ago in extending the system which was introduced in 1787 by Guyton de Morveau and Lavoisier and which has stood the test of time in remarkable manner. British,[1] German,[2] and American[3] versions of this report have been published in the journals of the chemical societies of Great Britain, Germany, and the United States, respectively. The editing of the British version, a translation of the original report in German, to bring spellings, spacing, and the like into conformity with approved American usage was done with the understanding that it was not the intention of the committee to interfere with the written forms peculiar to individual countries.

Reprints of the American version of the report can be obtained by sending ten cents in coin or postage to the undersigned. For a like price reprints can also be obtained of the older Definitive Report (rules for naming organic compounds). The price charged for these reprints is intended merely to cover the committee's expenses in obtaining and distributing them.

—E. J. CRANE, *Chairman*

NOMENCLATURE, SPELLING, AND PRONUNCIATION COMMITTEE
THE AMERICAN CHEMICAL SOCIETY
THE OHIO STATE UNIVERSITY, COLUMBUS, OHIO

[1] *J. Chem. Soc.*, **1940,** 1404–15.
[2] *Ber.*, **73A,** 53–70 (1940).
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The Unique Chemistry of Castor Oil

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STUDENTS of chemistry are well aware that vegetable oils—such as coconut, palm, cottonseed, and linseed oils—have for many years occupied an essential position in our industry as indispensable raw materials. A fundamental knowledge of their composition has allowed organic chemists to convert these naturally occurring triglycerides into a multitude of useful products. Among them might be mentioned the production of edible fat from cottonseed oil by hydrogenation and the manufacture from coconut oil of the higher aliphatic alcohols used to make the so-called soapless detergents.

All of the commonly used vegetable oils, including the four mentioned above, consist almost entirely of the triglycerides of long-chain aliphatic acids. Most of these acids contain seventeen carbon atoms plus the carboxyl group, and they differ from oil to oil principally in the number of olefinic bonds. For example, linseed oil contains a relatively large number of olefinic linkages and is a good drying oil for paints, while olive oil, with less unsaturation, is unsuited for such a purpose. Since the differences between vegetable oils are largely produced by variations in the number of double bonds, complete hydrogenation of the various oils should lead to quite similar types of hardened fats.

One of the most commonly used vegetable oils, castor oil, differs from others in that it contains a hydroxyl group in addition to an olefinic linkage in its predominating fatty acid. Ricinoleic (or 12-hydroxy oleic) acid forms about 80 per cent of the total fatty acid content produced upon saponification of castor oil. The structure of ricinoleic acid is as follows:

$$CH_3(CH_2)_5CHOHCH_2CH{=}CH(CH_2)_7COOH$$

The introduction of this hydroxyl group into the fatty acid chain gives castor oil many unique and interesting properties—both physical and chemical. One important physical property is viscosity, which in the case of castor oil is considerably higher than that of other fatty oils. Since viscosity is a measure of the ease with which the molecules are able to slide past one another, it seems likely that the hydroxyl groups may protrude from the fatty chains in such a way as to impede their free flow. Another extremely important physical property is solubility in various types of solvents, which in the case of castor oil is quite different from that of other fatty oils as a class. Castor oil tends to dissolve in oxygenated solvents like alcohols and not to dissolve in hydrocarbon-type solvents, while the reverse is true of other fatty oils. This peculiarity is also attributable to the presence of the hydroxyl group. From the synthetic point of view ricinoleic acid and castor oil have come to be considered as indispensable raw materials for a countless number of industrial applications in which no other fatty material could be used with equal success. We shall see that many of these can be traced to the presence of the hydroxyl group.

TYPES OF USES

Although castor beans in any desired quantity could be grown in the warm parts of this country, our present supplies are almost entirely imported from various parts of the world. In 1939 enough entered the country to allow the extraction of 73 million pounds of oil (*1*). This figure may be expected to increase considerably in view of the new large scale use as a starting material for making synthetic drying oils.

To the uninitiated the major outlet for castor oil is often thought to be medicinal. But the following estimate (*2*), averaging the 20-year period from 1918–38, indicates that this accounts for only a minor portion of the total consumption:

Use	*Per Cent*
Medicinal	8
Artificial leather	20
Sulfonated oils	25
Lacquers	10
Lubrication	17
Miscellaneous	20

ARTIFICIAL LEATHER AND LACQUERS

According to the above estimate about thirty per cent of all the castor oil produced is used for making artificial leather and as a lacquer ingredient. Both of these applications depend upon the superior properties of castor oil as a "plasticizing agent."

In the manufacture of artificial leather (*3*) a mixture of 25 per cent pigment, 25 per cent nitrocellulose, and 50 per cent castor oil is dispersed in a low-boiling solvent and applied to cloth. Upon evaporation of the solvent a tough leathery coating is deposited on the fabric. This process has been developed to a point where it is said to be difficult to distinguish artificial from genuine leather. It has been found that castor oil, when used in conjunction with nitrocellulose, yields a particularly satisfactory type of film with respect to strength and pliability. This is no doubt partially explained by the unusually high viscosity of castor as compared with other oils. In addition, the presence of the hydroxyl group endows it with a greater degree of miscibility with nitrocellulose than is the case with the other fatty oils, which do not have this structure. Apparently the effectiveness of any compound as a plasticizer depends to a considerable degree upon physical properties such as vapor pressure and miscibility with various resins and solvents. It should be noted that the ability of castor oil to function in this way depends upon its favorable physical properties rather than upon its chemical properties.

SYNTHETIC DRYING OILS

Paints contain vegetable oils, such as linseed or tung oils, which upon exposure to atmospheric oxygen form tough films covering the coated surface. This oxidation process is referred to as "drying," and linseed and tung oils are known as drying oils. They function as such because their fatty acids are highly unsaturated; for example, linseed oil contains a large percentage of the glyceride of linolenic acid, which contains three double bonds. Tung oil is also unsaturated, but it differs from linseed in that the double bonds of the former are conjugated, while those of the latter are not. Conjugated double bonds are generally known to be more reactive than an equal number of isolated ones, and it is found in practice that tung oil dries much more rapidly than linseed oil.

Castor oil contains only one double bond and does not have drying properties—that is, it does not react with atmospheric oxygen to form a paint film. A study of the structure of ricinoleic acid showed, however, that removal of the hydroxyl group as water would lead to the formation of a second olefinic linkage. This dehydration may be accomplished easily by heating the oil in the presence of water-splitting catalysts, which are usually weakly acidic materials such as sodium acid sulfate (*4*). The product, known as "dehydrated castor oil," contains two double bonds in each fatty acid chain, but not all the pairs appear to be conjugated, since dehydration can and does occur on either side of the carbon holding the hydroxyl group. It is interesting to note that the dehydrated castor oil (some conjugated double bonds) dries to a paint film more rapidly than linseed oil (no conjugated double bonds), but less rapidly than tung oil (mostly conjugated bonds) (*5*).

Why should chemists be so concerned with developing a synthetic drying oil when tung and linseed oils have proved so satisfactory? Most of the drying oils used in this country are imported from abroad—tung oil being introduced from China. The paint and varnish industry uses 87 to 120 million pounds of tung oil annually, and 95 per cent of this quantity comes from China (*6*). During the present war the price of tung oil has risen and the exports from China have been rendered quite uncertain, with the result that paint manufacturers have been forced to look for a substitute capable of domestic production. Dehydrated castor appears to be a promising answer.

LUBRICANTS

Before the introduction of mineral oils during the second half of the last century, almost all lubrication of moving mechanical parts was accomplished by the use of fatty oils. In general it was observed that these gave quite satisfactory performance for the primitive requirements of that time, but in particular it was found that castor oil gave particularly smooth lubrication, especially for engines operating at high speeds for only short periods of time. Early types of racing and airplane engines operated smoothly with castor oil for a short interval provided that piston temperatures remained moderate. It was found, however, that continued use of castor oil in the same engine resulted in the breakdown of the fatty oil, with the formation of a sticky resinous mass that rendered the engine almost useless. With the development of higher speed engines, operating at higher temperatures, this difficulty became more urgent, but the improvement of mineral lubricants with their subsequent adoption for high output motors solved the problem while rendering castor oil obsolete. But in spite of this general adoption of petroleum oils castor is still used for engine lubrication. New engines are sometimes "broken in" with castor oil before the change to mineral oil is made, and it has been observed that the quality of "oiliness" possessed to a high degree by castor persists for a remarkable length of time after the shift has been made (*7*).

Modern lubrication theory suggests that polar molecules, such as fatty acid esters, are efficient lubricants because their functional groups allow orientation at the surface of the bearing—with the resultant formation of a tenacious film which at the same time reduces friction. The presence of the hydroxyl group makes castor oil even more polar than the usual type of fatty oil, and for this reason it might be expected to possess considerably greater oiliness (power to reduce friction).

Since mineral oils consist almost entirely of non-polar hydrocarbon molecules they possess little oiliness compared to fatty oils—and particularly little compared with castor. Mineral oils, however, are stable and do not decompose so objectionably. It might be thought possible to combine mineral oil with castor in such a way as to obtain a stable lubricant with high oiliness (*8*). Unfortunately the hydroxyl group—which gives castor oil its enhanced oiliness—also renders it insoluble in mineral oils. Chemists have gone to considerable effort to obtain miscibility, but the results to date have not proved particularly satisfactory. One method of attack has been the use of a mutual solvent for the two types of oils. Another method, said to be in commercial production in Brazil (*9*), involves the application of the emulsifying agent triethanolamine. Heating and air blowing also improves its mineral oil solubility, but the resulting blend is said to be rather unsatisfactory, perhaps because during the heating process some of the oiliness-producing hydroxyl groups are removed as water.

The resinous materials formed from castor oil upon prolonged use as a lubricant no doubt arise partly as a result of dehydration upon the hot metal surfaces of the motor. Air, which is always present in engines, would then cause the dehydrated oil to "dry" as in the case of paint films. The easy dehydration of castor oil can hardly be looked upon as an unmitigated advantage.

WETTING AGENTS

Wetting agents, in general, are made by uniting in one molecule a water-soluble group (such as sulfate) and an oil-soluble group (such as a long paraffin chain). Castor oil is a convenient raw material from which to make

such products because water-soluble groupings may be easily introduced by manipulating the hydroxyl group already attached to the paraffin chain of the fatty acid.

Castor has long been employed in the manufacture of "turkey-red oil"—a material so called because of its use with red alizarin dye as a wetting and penetrating agent. Turkey-red oil is produced by treating castor oil with strong sulfuric acid, followed by neutralization with alkali. The product so formed enables dyestuffs to penetrate cloth fibers, and, once having penetrated, to cling more tenaciously. The exact chemical nature of turkey-red oil is still unknown, and its method of manufacture is an art, but something is known of the types of reactions occurring during its formation. The hydroxyl group is probably esterified with the formation of an alkyl sulfuric acid, while another sulfuric acid molecule may add across the olefinic double bond (*10*). Solubility in aqueous solvents is determined by the proportion of sulfate groups present, which is in turn decided by the conditions under which the sulfation is conducted. Turkey-red oil is still widely used by dyers, although many of the recently developed special-purpose wetting agents are encroaching upon its field.

PERFUMES AND FLAVORS

The reactions discussed up to the present have been largely the conventional ones of the hydroxyl group alone, its position in the paraffin chain being secondary. We are now ready to consider a rather unorthodox type of reaction involving both the double bond and the hydroxyl group. The products so formed are of particular interest to the synthetic chemist since from them a wide variety of valuable compounds may be prepared.

When castor oil is heated *in vacuo* decomposition of the ricinoleic portion occurs, with the production of heptaldehyde and undecylenic acid as follows:

$$CH_3(CH_2)_5CHOHCH_2CH{=}CH(CH_2)_6COOH \rightarrow CH_3(CH_2)_6CHO + CH_2{=}CH(CH_2)_8COOH$$

Both of these compounds are extensively used as raw materials for the manufacture of perfumes and flavors (*11*).

Upon oxidation heptaldehyde is converted to heptoic acid, the ethyl ester of which is widely used as a perfume material—over three and a half tons being produced in 1939 (*12*).

When heptaldehyde reacts with benzaldehyde in the well-known aldol reaction, amyl cinnamic aldehyde is produced as follows:

$$C_6H_{11}CH_2CHO + C_6H_5CHO \longrightarrow C_6H_5CHOHCHCHO \xrightarrow{-H_2O} C_6H_5CH{=}CCHO$$

(with C_5H_{11} on the CH and C_5H_{11} on the CCHO)

Thirty-four tons of this material were manufactured in 1939 (*12*).

The undecylenic portion of the castor oil molecule also finds wide use in the manufacture of flavoring materials. Undecalactone, widely employed as a peach flavor, may be synthesized as follows:

$$CH_2{=}CH(CH_2)_8COOH \xrightarrow{H_2SO_4} CH_3(CH_2)_6CH{=}CHCH_2COOH \longrightarrow CH_3(CH_2)_6CHCH_2CH_2$$

(with O—CO)

By employing a different type of cleavage reaction, conducted under alkaline conditions, we may obtain capryl alcohol and sebacic acid as follows:

$$CH_3(CH_2)_5CHOHCH_2CH{=}CH(CH_2)_7COONa \xrightarrow{NaOH} CH_3CHOH(CH_2)_6CH_3 + NaOOC(CH_2)_8COONa$$

The alcohol is employed as such and as the butyrate and acetate in perfumes, as is also its oxidation product, methyl hexyl ketone. Ethyl sebacate is used in flavors.

From heptaldehyde may be synthesized methyl heptine carbonate, which is widely used as a constituent of violet perfumes:

$$C_6H_{11}CH_2CHO \xrightarrow{PCl_5} C_6H_{11}CH_2Cl_2 \xrightarrow[KOH]{-2HCl} C_6H_{11}C{\equiv}CK \xrightarrow{ClCOOCH_3} C_6H_{11}C{\equiv}CCOOCH_3$$

The corresponding octine ester may be made from methyl hexyl ketone.

In the accompanying table are shown a number of additional compounds which may be derived directly or indirectly from castor oil. As time goes on organic chemists are finding many of these compounds increasingly essential in making many useful materials, a number of which are briefly indicated.

Castor oil appears to be in the ascendency as a raw material for our chemical industries. This has been made possible largely by an understanding of the chemical composition of the oil, and by a corresponding knowledge of what types of structures are required for specific uses. It is hoped that this brief review of its chemistry may provide an understanding of further uses as they appear.

CHEMICALS DERIVED FROM CASTOR OIL

Substance	*Method*	*Use*
Dibasic acids:		
Suberic—$HOOC(CH_2)_6COOH$	Sodium ricinoleate fusion	Synthetic fibers
Azelaic—$HOOC(CH_2)_7COOH$	Ricinoleic oxidation	Synthetic fibers
Sebacic—$HOOC(CH_2)_8COOH$	Ricinoleic oxidation	Synthetic fibers
Monobasic acids:		
Heptoic—$C_6H_{13}COOH$	Heptaldehyde oxidation	Synthesis
Nonylic—$C_8H_{17}COOH$	Sodium undecylenate fusion	Synthesis
Undecylic—$C_{10}H_{21}COOH$	Cracking of castor oil	Synthesis
Undecylenic—$C_{10}H_{19}COOH$	Cracking of castor oil	Synthesis
Hydroxy stearic—$C_{17}H_{34}OHCOOH$	Ricinoleic reduction	Synthesis
Heptaldehyde—$C_6H_{13}CHO$	Cracking of castor oil	Perfume synthesis
Capryl alcohol—$C_8H_{17}OH$	Sodium ricinoleate fusion	Perfume synthesis.
Isobutyl undecylenamide—$C_{10}H_{19}CONHC_4H_9$	Heat undecylenic acid and isobutyl amine	Insecticide (*13*)

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Optimum Volume for a Wash Portion[1]

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IT IS common knowledge among analytical chemists that a precipitate should be washed with several small portions of the wash liquid with complete intermittent drainage, rather than with one or two large portions of the liquid. No adequate discussion of the precise amount of wash portion required is available.

Equations of the following type have frequently been derived:

$$\frac{x_0}{x_n} = (1 + v/u)^n$$

where x_0 is the amount of impurity before any washing, x_n the amount of impurity after n washings, v the volume of each of the n portions, all equal, and u the volume of wash liquid retained by the pores of the precipitate and between it and the walls of the vessel; hereafter this will be referred to as the "absorption volume."

Some authors have substituted arbitrary figures in such equations in order to compare the theoretical, relative effectiveness of different size wash portions for a single, isolated, imaginary case, but the only general analysis of the equation which appears to be available is that of Gerald E. Marsh.[3] Marsh's summary is an able and comprehensive one, but it contains several minor inaccuracies and inconveniences for the purpose of the present discussion: where, for instance, we refer to the "absorption volume" he speaks of the "total volume of the precipitate"; instead of using the phrase "the volume of the individual wash portion," Marsh refers to "the total volume of the containing vessel" meaning, presumably, the sum of the absorbed volume and the volume of the wash portion. When he says "the solution of the problem centers around the determination of the number of washings necessary to reduce the impurity by the desired amount and the volume of wash water required for the process," he makes an error that is also common to other treatments of the equation, for it can readily be shown that the relative effectiveness of the different size wash portions depends not at all on the degree of purification expected by the analyst.

To demonstrate this, the original equation,

$$x_0/x_n = (1 + v/u)^n \tag{1}$$

is simplified for convenience in manipulation to

$$p = (1 + r)^n \tag{2}$$

where x_0/x_n becomes p and is called the "purification ratio" and where v/u becomes r and is called the "washing ratio."

The logarithmic form further simplifies it:

$$\log p = n \log (1 + r) \tag{3}$$

and the number of washings is

$$n = \log p/\log (1 + r) \tag{4}$$

The principal value of a study of this equation is the discovery of a technic that will save as much wash liquid as possible. Therefore, it is desirable to translate equation (4) into one in terms of the total volume of wash liquid desired:

Let

V = this total volume of wash liquid

Then

$V = nv$, the number of wash portions times the volume of each portion

Multiplying equation (4) by v gives

$$nv = V = v[\log p/\log (1 + r)] \tag{5}$$

[1] Presented before the section of Analytical and Inorganic Chemistry of the Division of Physical and Inorganic Chemistry at the ninety-fifth meeting of the A. C. S., Dallas, Texas, April 20, 1938. An adaptation from the Dissertation presented to the Graduate College of the State University of Iowa by W. P. Cortelyou for the Ph.D. degree in August, 1937.

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r has been defined as v/u, so $v = ur$ and we have

$$V = ur[\log p/\log (1 + r)] \quad (6)$$

A useful approach would be to consider as a reference case the washing of a precipitate with portions that are the same size as the volume absorbed by the precipitate. In other words, the case where $v = u$, or $r = 1$. In this case the general equation (6) becomes the specific equation,

$$V_1 = u (\log p/\log 2) \quad (7)$$

The question may now be posed: How does the total volume of the wash liquid used in any given case compare with the volume which would be used in the reference case? This question may be answered with an equation derived by dividing equation (6) by equation (7) with the result:

$$V/V_1 = r[\log 2/\log (1 + r)] \quad (8)$$

which demonstrates (since log p cancels out of the expression) the expected purification has nothing to do with the relative amount of wash liquid required, and to consider it in the discussion, as previous writers have done, is only to confuse the issue.

The application of this equation is best appreciated by studying Table 1 which was derived from it.

TABLE 1

$\log_2 r$	r	V/V_1
$-\infty$	0	0.69
−3	1/8	0.73
−2	1/4	0.78
−1	1/2	0.85
0	1	1.00
1	2	1.26
2	4	1.72
3	8	2.52

Suppose that a given precipitate is washed to the desired purity with wash portions equal in size to the absorption volume of the precipitate (the reference case). The table shows what would happen if the precipitate were washed *to the same degree of purity* with the size of the wash portions cut in half. It shows that the total volume of the wash liquid required would be 85 per cent of that required in the reference case. If the experiment were repeated with the size of the wash portion cut in half again, then the total volume of the wash liquid would drop only to 78 per cent of that required in the reference case. If the halving were repeated the drop would be only to 73 per cent, and if infinitely small portions were used the total volume required would still be nearly 70 per cent of that required in the reference case. Evidently, then, reducing the size of the wash portion beyond that point at which $r = 1$ saves little wash liquid, and even this (as will be shown later) is at the expense of a large increase in the number of operations required.

Referring again to the table: doubling the volume of each portion will mean the use of 26 per cent more water; using portions four times the original size (doubling it again) will make the total consumption 72 per cent larger, and using portions eight times as large as the original (doubling it a third time) will mean a total volume of more than 2.5 times that used when $r = 1$.

If it is desired to plot these values, it can be done conveniently by plotting them against the logarithm of r to the base 2, which is given in the table and indicates the number of times the wash portion is halved or doubled.

A study of the total volume of wash liquid required is of little value without showing at the same time how a change in the size of the wash portion affects the number of operations involved.

These data are obtained from equation (4):

$$n = \log p/\log (1 + r) \quad (4)$$

and from the special case in which $r = 1$,

$$n_1 = \log p/\log 2 \quad (9)$$

Dividing (4) by (9) gives

$$n/n_1 = \log 2/\log (1 + r) \quad (10)$$

which, in conjunction with equation (8), gives the very simple relation:

$$n/n_1 = (1/r) V/V_1$$

by means of which Table 1 is easily expanded into Table 2.

TABLE 2

$\log_2 r$	r	V/V_1	n/n_1
	0	0.69	∞
−3	1/8	0.73	5.87
−2	1/4	0.78	3.10
−1	1/2	0.89	1.71
0	1	1.00	1.00
1	2	1.26	0.63
2	4	1.72	0.43
3	8	2.52	0.31

From this table it is seen that though cutting the washing ratio from 1.00 down to 1/8 saves less than 30 per cent of the total wash liquid, to do so would involve almost six times as many washing operations.

On the other hand, raising the washing ratio from 1 to 2 will take only 26 per cent more water, but it will reduce the number of operations more than one-third, and raising it to 4 will require only 70 per cent more water, but will reduce the number of operations to considerably less than one-half the number originally required.

Whether emphasis is to be placed on keeping the total amount of washing liquid at a minimum, or on using a minimum number of operations is a matter which must be decided in each individual case, but it becomes obvious that the general rule of washing with 10-cc. portions (which is not at all uncommon)takes entirely too much for granted. If one must take the risk of generalizing (and that is extremely hazardous), it would be better to say that the wash portion should be from two to four times as large as the absorption volume of the precipitate. This volume will frequently be considerably less than 10 cc. for the typical analytical precipitate.

It must be noted that this discussion is based on two assumptions: (1) that these simple equations apply to the actual washing of precipitates, and (2) that it is possible to estimate the absorbed volume with reasonable precision.

High-School Chemistry

Some Suggestions for Science Teaching in the High School[1]

R. H. WRIGHT *University of New Brunswick, Fredericton, New Brunswick, Canada*

HIGH-SCHOOL science courses seem to me to have a threefold objective. First, they should give students an understanding of the scientific attitude real enough and vivid enough to be carried over into everyday life. Then, too, our science courses ought to bring out very clearly the close relations and interactions between science and society, so as to break down the artificial barriers which at present surround scientific activities. Finally, we should make it possible for the average educated person to follow intelligently current scientific developments, partly for the personal satisfaction to be gained thereby and partly in the hope of hastening the application of new knowledge to increasing human welfare and happiness.

If the general public were more familiar with science in the way suggested, the path of progress would be a vastly smoother one. For example, it would be difficult for selfish or reactionary interests to hold up the application of new discoveries in the face of a widespread realization of the contributions science is capable of making. At the same time, it would be possible to anticipate the social stresses and widespread readjustments that so often follow innovations in agriculture and industry and communication, and so make provision in advance for those who must otherwise suffer through no fault of their own.

Taking, then, as the three objectives of our science courses, the inculcation of a scientific outlook, the breaking down of the barriers around science, and the dissemination of an understanding of what science offers to humanity, let us see what form the high-school science courses can usefully take.

It will be clear at once that, given these as our objectives, no distinction is necessary between those students who are going on to college and those who are not. Thus at one blow we eliminate what has been a source of worry to many teachers.

What the scientific method really is has been the subject of a good deal of discussion—much of it beside the point. The best course for us to pursue is to ask ourselves what characteristics distinguish the best type of scientific worker, and then try to see how these qualities may be developed. This is so because the scientific method really boils down to a state of mind.

The first quality which we must seek to bring out is a capacity for careful and patient observation coupled with a scrupulous attention to the meanings of the words used in describing what we see. I would suggest that an extremely useful series of laboratory exercises could be based on the collection of specimens of matter for examination and study. For example, a class might collect samples of different kinds of metal: iron, aluminum, brass, bronze (a cent), lead, zinc (from an old dry cell), and so forth. They should then examine each specimen, noting the similarities as well as the differences, and try to frame unambiguous and specific descriptions of each kind of matter. It might be a good idea for half the class to collect, describe, and classify samples of metal while the other half did the same for samples of rock or wood or cloth. The two sections could then exchange samples and descriptions and each try to identify the substances to which the descriptions were supposed to apply. This work would lead naturally to the introduction of such physical concepts as density, hardness, etc., and to various simple chemical tests such as reaction with acids or alkalies, ease of corrosion, and so forth. It would also show the gain in precision and economy of words that follow from using quantitative data whenever possible.

Knowing the source of each sample, the students would come to realize how a knowledge of the properties of matter enables each kind to be put to the best use, and in this way some point would be given to the descriptive matter which so many students regard as inexpressibly tiresome because it seems so futile. Also, the need for care and precision in the use of words would cease to be an irritating bit of pedantry by becoming a matter of common-sense necessity. Care should be taken, however, to point the moral of this, for it seems that a great many people fail to transfer ideas from one field of thought to another, perhaps because they do not happen to think of it. Most of the discussion of matters of national importance would be rendered far more useful if greater clarity were attached to the words used and the epithets applied.

Turning now to ways in which the intimate interactions of science and society can be brought out, we find it valuable to try to see each scientific discovery and technical innovation against its historical background. Take, for example, the manufacture of washing soda. Since ancient times, sodium carbonate has been used in making soap, in the manufacture of glass, and for removing the grease from wool before spinning it into yarn. For centuries adequate supplies of soda could be obtained from the ashes of seaweed or from natural

[1] Presented before the Science Section of the New Brunswick Teacher's Association, Fredericton, New Brunswick, Canada, April 17, 1941.

deposits in Egypt and other dry countries. With the growth of towns and the necessities of building that accompanied the industrial revolution, with the appearance of national armies clothed in woolen uniforms, and with the ever present danger of wartime stoppage of sea-borne commerce, it became important to devise more abundant and, if possible, blockade-proof sources of this chemical. Kier's soda process, developed in 1780, and the more famous LeBlanc process of 1791 take on a new interest and a new significance when seen against this background. And the more general tendency of which this is but one example, the urge to find new supplies of needed materials, had a profound effect in shifting the direction of chemical inquiry from the qualities of things to their composition, for only by so doing could new resources be tapped. This change in the outlook of chemists led to the Laws of Definite and Multiple Proportions and culminated in Dalton's theoretical synthesis which ushered in the modern period of chemical science.

Or again, take the discovery of the material nature of gases, surely one of the most epoch-making of human achievements and worthy of rank with the invention of the wheel and of written language. For thousands of years only solids and liquids were regarded as matter: what we call gases were "spirit"—"spirit" in the sense of "spook." So long as processes like distillation were thought of in terms of a transformation of substance into spirit, and so long as the atmosphere was left out of account in chemical investigations, just so long was the Law of the Conservation of Mass beyond human comprehension and modern chemistry and technology impossible of achievement. The realization that gases are a third state of matter did not come all at once; it emerged. It emerged gradually from the background of historical circumstance. On the one hand the needs of deep-sea navigation by the stars led to Newton's theoretical work on the Laws of Motion, the central idea of which was force. Now force was associated with matter and the force of the wind on the sails of ships suggested almost irresistibly the materialness of air. Then, too, problems of mine ventilation drew attention to the differences between good and bad air, explosive and safe mine gas. True, men had been digging mines for a long time, but in the old days mining was a job for slaves whose lives and well-being were of little or no account. When Christianity had abolished slavery in western Europe and the Black Death had ended its epilogue in serfdom, when gunpowder and the wars of religion swelled the demand for coal and iron, then a generation of free and independent miners could demand and obtain consideration for their health and safety.

These are examples of the way society has determined the direction of scientific research and the course and intensity of its development. The interactions from the other direction are just as close. Thus it is probable that the Greeks of classical antiquity failed to extend their primitive democracy beyond the limits of the city state partly because the number of people who could participate in democratic processes was limited to the number who could assemble within hearing distance of a single speaker. At any rate, this is a more rational explanation than the suggestion that there was some fatal defect in the Greek character. Parliamentary government in England remained in a state of arrested development until the printing press made it possible for an individual to speak to an entire kingdom. The extension of democratic institutions to embrace a whole continent was only possible in the United States and Canada because the telegraph was coupled with the printing press. Coming down to the present, the radio and the airplane seem to open the way to profoundly important innovations within our Commonwealth and, indeed, throughout the world. It needs, however, a general awareness that things are possible now that were never possible before if we are to overcome the memory of past failures. We can make a very large contribution to the advancement of democratic ideals by preparing people's minds for the full utilization of the material resources that science places at our disposal.

The organization of scientific knowledge, the union of generalizations and hypotheses with a cement of logic into the closely articulated structure of theory uniting all scientific knowledge, is something calling for the clearest and most careful exposition. Elsewhere[2] is given a conception of the pattern of scientific knowledge which will not be repeated here. But we would like to suggest that the best method of presenting it has still to be worked out. It is probably better to delay its full exposition until the students are familiar with one or two examples of scientific theories, say Dalton's atomic theory and the kinetic theory of gases. By using these as examples the exposition can follow the usual course of scientific development: from the particular to the general and back again to the particular.

If students could be trained to analyze a theory, to appraise its simplifying assumptions and check its logic, if they were able to distinguish clearly between generalization and hypothesis and apply the proper criteria to each, they would be given a training of inestimable value in times like these when the world is being re-made and the democracies are at the parting of the ways.

In this connection, several useful suggestions concerning laboratory work can be made. It is clearly impossible for high-school students, or anyone else, to test personally every generalization and every statement of fact that is presented to them. What they can do, and what they should be encouraged by every means to do, is to pick out those that are critically important and to devise tests they can apply themselves. Where this personal testing is beyond the range of their skill or resources, they should learn to examine critically the written accounts of the experiments of others. For their own experiments it is not always necessary for them to use ready-made or expensive apparatus. In fact, up to a point we can make a virtue of necessity by

[2] WRIGHT, "The nature and organization of scientific knowledge," J. CHEM. EDUC., **17**, 270–3 (1940).

having our students exercise their ingenuity in devising their own apparatus and experiments. For example, a homemade spring balance improvised from a coil of wire and a yardstick will serve to test the Law of Definite Proportions or Conservation of Mass as well as and maybe better than an expensive and unfamiliar balance. Moreover, by proceeding in this way we shall break down the idea that the scientific method is inseparable from intricate and costly apparatus, and so make it what it really is—a state of mind.

Then, too, the ideas of precision of measurement and experimental error, a grasp of which is of first importance, can be brought out by making the experiments simple enough for each to be repeated a number of times. There is no better way of showing how the results of supposedly duplicate measurements are scattered about a central value, and of bringing out the significance of a mean value. This is very important because so many people have the impression that science is absolutely exact, and that what is not exact is not science. Actually, science involves the practical utilization of data which are not and never will be absolutely exact but which are as exact as care and existing resources can make them. If students entering college were vividly aware of this, the task of giving them a professional training in the use of modern laboratory appliances would be made enormously easier. They would realize from the outset that complex apparatus and the experiments they perform are a means to an end rather than an end in themselves.

Yet another advantage of keeping chemicals in fancy packages and ready-made apparatus at a minimum is the opportunity it would provide for bringing out the collective aspect of scientific work. A model scientific journal could be mimeographed at small cost and in it groups of pupils could publish accounts of their experiments and conclusions. In this way the experience of each group would be made available to all, the practice of consulting the technical literature could be fostered, and we would have in fact an actual model of science at work.

An important function of such a journal would be to accustom students to having their experimental methods criticized, their conclusions pulled to pieces, and perhaps their personal feelings temporarily hurt. In the rough and tumble of such discussion they would come to realize that scientific research is the most democratic occupation in the world in that it demands the fullest and frankest discussion of every point, the elimination of all sloppy thinking, and the appeal to experience in case of doubt or uncertainty or disagreement. They would learn that the advancement of knowledge requires the sacrifice of personal feelings and prejudices.

Then, too, such a journal might serve to bring home to students a realization of the mighty contribution that has been and always will be made by a multitude of unsung and largely unknown privates in the army of scientific workers, the men and women who, by their patient, unspectacular filling of a gap here and correction of a mistake there, provide in the aggregate the wealth of comprehensive and reliable data on which are based the great theoretical syntheses and spectacular technical innovations.

Imagine, if you can, the moral and material consequences of transforming this country into one vast experimental farm, with every farmer making his individual contribution to our collective knowledge by careful observations of, say, the effects of various methods of soil improvement, or new methods of stock feeding or pest control, or the acclimatization of new species. The feeling of working together and the new interest in everyday tasks which would be developed would, we believe, bring a new life and a new spirit to this country.

The reader may, perhaps, feel that many of these suggestions lie outside the normal range of the high-school science teacher, and that training in clarity of expression and the exact use of words are the province of the teacher of English while the interrelations of science and society are matter for history lessons. With this we cannot agree. The bad effects of this tendency to parcel out knowledge in specialized compartments beset the educational process at every stage and are better combatted early than late.

Finally, let us urge an emphasis at every turn upon the living, developing, and ever changing scope of scientific knowledge. Science is neither perfect, nor final, nor exact. The best type of scientific mind is always open to new ideas, and ever willing to consider the most profound revisions of accustomed notions whenever new additions to knowledge shall call for them. Many people seem to think that to be scientific they have only to be skeptical. The truth is that while skepticism is necessary it is by no means sufficient, and that too often a pseudo-scientific skepticism is no more than a cloak for cynical indifference. The true scientific worker is generally a skeptic but he is enthusiastic in his skepticism and seeks actively to find in experience the solution to his doubts. Then again, scientific caution and suspended judgment sometimes slide insensibly into a state of suspended animation. The true spirit of science is not found in suspended judgment, which is a negation, but rather in the negation of this negation, in reaching admittedly provisional and imperfect conclusions and using them as stepping-stones in the lively and exciting business of using our collective brains to improve our collective environment.

DEMONSTRATION INVOLVING AIR PRESSURE

G. M. LISK

Northwestern State College, Alva, Oklahoma

THE absorption of ammonia in water may be demonstrated by the apparatus in Figure 1. The ammonia is prepared by boiling concentrated ammonium hydroxide and passing the gas through Drierite. Upon pressing the bulb of the medicine dropper, the balloon swells. Shaking the flask hastens the action. HCl gas may be used instead of NH_3.

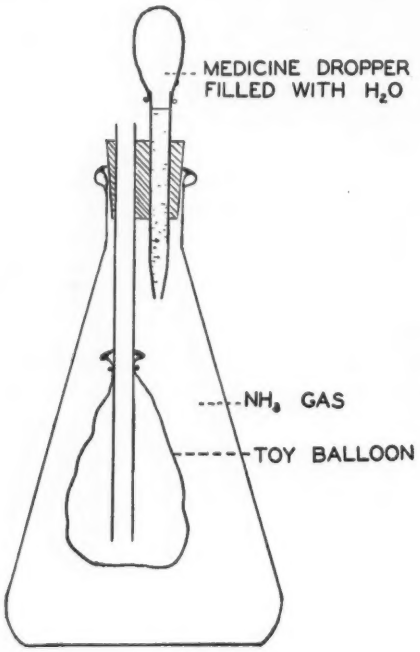


FIGURE 1

The creation of a vacuum when steam is condensed may be illustrated by the same apparatus. Boil a little water in the open flask; remove the burner; insert the stopper carrying the medicine dropper and balloon. Press the bulb, and as the steam condenses, the balloon swells.

Action of an air pump may also be demonstrated by replacing the medicine dropper by a length of glass tubing attached to an air pump.

SUMMER CHANGE OF ADDRESS

UNTIL September 5, all correspondence for the Editorial Office of the JOURNAL should be addressed to: JOURNAL OF CHEMICAL EDUCATION, WOODS HOLE, MASSACHUSETTS.

LETTERS

Another Mnemonic

To the Editor:

H. H. Hatt's letter in the April, 1941, issue of the JOURNAL OF CHEMICAL EDUCATION concerning a rule for remembering that caproic, caprylic, and capric acids constitute the sixth, eighth, and tenth members, respectively, of the fatty acid series reminded me of this mnemonic which I used when I was in college to remember the names of the first eleven normal fatty acids containing an even number of carbon atoms.

The trivial names of all the normal fatty acids with an even number of carbon atoms, from acetic acid through stearic acid, begin with letters which occur in normal alphabetical sequence, as may be seen from the list below:

1.	Acetic	C_2
2.	Butyric	C_4
3.	Caproic	C_6
4.	Caprylic	C_8
5.	Capric	C_{10}
6.	Lauric	C_{12}
7.	Myristic	C_{14}
8.	Palmitic	C_{16}
9.	Stearic	C_{18}

The two acids immediately following stearic acid in the above series are **A**rachidic, C_{20}, and **B**ehenic, C_{22}, in the order named, and here again the initial letters of the trivial names fall in the sequence of the alphabet.

If **O**leic acid, with its sixteen carbon atoms, belonged to the above series it, too, would fall in alphabetical order just after **M**yristic acid and just before **P**almitic acid.

W. T. SUMERFORD

SCHOOL OF PHARMACY
UNIVERSITY OF GEORGIA
ATHENS, GEORGIA

Large Crystals

To the Editor:

The recurring appearance of articles on the growing of chrome alum crystals suggests that some of your readers might be interested in a note regarding the following procedure, which I cannot recall seeing written up anywhere.

Large crystals which require no protective coating may be grown in solutions containing approximately equal weights of potassium chrome and potassium aluminum alums. I have had one about three inches in diameter on my desk for six years without noticeable efflorescence. The depth of color of such crystals may be varied by changing the amount of chrome alum in solution, giving a good demonstration of the formation of solid solutions.

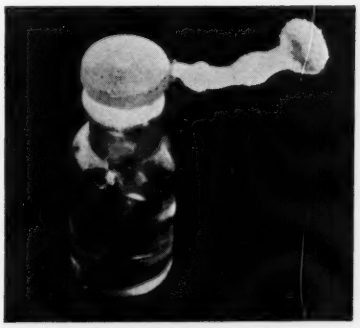
R. P. SEWARD

PENNSYLVANIA STATE COLLEGE
STATE COLLEGE, PENNSYLVANIA

Out of the Editor's Basket

THE problem of the survey or general course in chemistry is a recurrent one. J. W. Neckers tells us that their experience at Southern Illinois State Teachers College shows that such a course can be adapted both to the general student and to the one who plans to continue in chemistry. This is done by the arrangement of the course rather than by any novel sort of content. The quantitative and more "technical" topics are left to the third term while the more general and descriptive matter is taken up in the first two terms, after which most of the general students drop out, leaving the more serious ones to struggle with the stronger meat. Topics taken up at this later time include: a review of the gas laws, molecular and atomic weights, equilibrium and the mass law, solubility products and ionization constants, the Debye-Hückel theory of electrolytes, normal solutions, electrochemical theory, oxidation-reduction equations, especially applied to nitrogen, sulfur, and the halogens.

The first two, "general" terms are of course not entirely devoid of fundamental theory and include enough discussion of atomic structure to make the subject of valence rational. However, the quantitative and mathematical treatment does not go far beyond the laws of chemical combination and simple stoichiometric calculations. There is accordingly time for a more adequate consideration of the metals and of organic chemistry than is usual in an elementary course.



AN AMMONIUM CHLORIDE GROWTH, ON A HYDROCHLORIC ACID BOTTLE

● Since publishing last month an illustration of a striking growth of ammonium chloride we found in our own laboratory an even more remarkable case. As the accompanying illustration shows, it was in the form of a long tube with a flare at the end like the mouth of a cornet, more than two inches long, extending from the neck of a small bottle of concentrated hydrochloric acid. It started, evidently, from a spot where HCl escaped from under the glass stopper, into an ammonia-laden atmosphere. It looked very much like a piece of small tubular lamp-wicking, of irregular diameter.

● H. W. Schneider, of the Varniton Company, has sent us some interesting notes concerning demonstrations of chemiluminescence. A substance called "Catalyst A" (a Werner-complex compound of poorly understood structure) has been prepared which catalyzes the oxidation of luminol, 3-amino phthalhydrazide. The use of this latter substance to produce chemiluminescence, by reaction with hydrogen peroxide and potassium ferricyanide, was described some time ago.[1] Catalyst A

Photo by Walt Disney Studios

CHEMILUMINESCENCE OF LUMINOL AND "CATALYST A"
Note the curious effect on the fingers of the hand gripping the sponge from which the luminous solution is being squeezed

not only can be substituted for potassium ferricyanide in all these reactions but produces its effect in an alkaline solution of luminol even in the absence of hydrogen peroxide. It would seem that under these circumstances the oxidation is brought about by atmospheric or dissolved oxygen.

Among the advantages claimed for the use of this catalyst are the extraordinarily small amount necessary and the long persistence of the light produced. Brilliant light effects were said to be possible in the sea at night, and upon snow and ice. Some slight variations in the usual luminol demonstrations were suggested: (1) Put the alkaline luminol and H_2O_2 solution in a tall cylinder and sprinkle Catalyst A on the surface to produce long luminous streamers. (2) A sponge soaked in luminol solution with Catalyst A added. Squeezing out the water produces the effect noted in the illustra-

[1] HUNTRESS, STANLEY, AND PARKER, J. CHEM. EDUC., **11**, 142 (1934).

tion. (3) Luminol solution with Catalyst A poured over snow in a dish. (4) Color effects by addition of fluorescein or Rhodamine B.

Luminol solutions may be prepared as described in the paper cited or by dissolving 0.4 g. in a little saturated Na_3PO_4, adding 40 ml. of three per cent H_2O_2, and diluting to one liter. Catalyst A may be had from the Varniton Company, 5025 West Washington Boulevard, Los Angeles, California.

● Something about tin cans came to our attention the other day. It seems that out of our annual consumption of about 80,000 tons of tin some 25,000 tons go onto the scrap heap on tin cans. With the possibility of a tin shortage one might wonder whether this waste could be profitably saved. Cans are sometimes reclaimed for the iron they contain, but not the tin. Its recovery is too expensive to make the process profitable.

● We have recently received a copy of the second progress report of the A. C. S. Committee on Carbohydrate Nomenclature. Twenty-one rules of nomenclature have been agreed upon and the Committee requests careful consideration of them on the part of anyone interested, before they are submitted for final adoption. Copies of the report may be had from the chairman, Charles D. Hurd, Northwestern University, Evanston, Illinois.

RECENT BOOKS

APPLIED CHEMISTRY FOR ENGINEERS. *E. S. Gyngell,* Ph.D., B.Sc., Lecturer in Applied Chemistry, Northampton Polytechnic, London. Edward Arnold and Co., London; Longmans, Green and Co., New York City, 1940. viii + 328 pp. 135 figs. 14 × 21.5 cm. $4.00.

The purpose of the book is to explain the chemistry of certain materials and processes which are of importance to the engineer. The text is divided into six sections as follows: Section 1, Fuels and Combustion, 177 pp.; Section 2, Metallic Corrosion, 48 pp.; Section 3, Paints and Varnishes, 11 pp.; Section 4, Water Treatment and Sewage Disposal, 40 pp.; Section 5, Cements, 14 pp.; Section 6, Lubrication, 12 pp. The book is written so that those with very little training in chemistry will be able to understand the material, and the topics have been picked by the author as those having primary interest for the engineer. The size of each section has been determined by the author's opinion of its importance to the general engineer.

It would be hard to obtain general agreement on the topics to be included in a book with the aims stated by the author, but accepting the distribution presented, the purpose of the book has been fulfilled. It is doubtful if any of the topics, except possibly Fuels and Combustion, would give the engineer any more than a mere introduction. They would, however, give him a starting point for further reading if he desired to cover the subject more thoroughly. The references are primarily English publications, and for a book of this type it would seem that they should be much more extensive.

From the viewpoint of chemical education, it is rather difficult to see where this book would fit in with the standard courses in chemistry or chemical engineering. It would be useful for assigned reading in courses in other branches of engineering.

The book is well written, and many excellent graphs and figures are presented.

ARTHUR A. VERNON

NORTHEASTERN UNIVERSITY
BOSTON, MASSACHUSETTS

THE HUMAN WORTH OF RIGOROUS THINKING. *C. J. Keyser,* Adrian Professor Emeritus of Mathematics, Columbia University. Third Edition. Scripta Mathematica, New York City, 1940. vi + 323 pp. 13.5 × 21 cm. $2.50.

The book consists of seventeen addresses and essays from the early years of this century, first collected in 1916, and republished in 1925. By "rigorous thinking" the author means mathematics, and most of the book is devoted to its praise.

Whoever braves Professor Keyser's esoteric and polysyllabic vocabulary will experience throughout the pleasure always obtainable from listening to an enthusiast. He actually believes that mathematics is as engrossing and beautiful as chemistry!

The content of these essays is by no means limited to eulogy of "the universal art apodictic"; many other stimulating and valuable ideas are put forth. The chapter on "The Permanent Basis of a Liberal Education" is particularly to be recommended. In it the author refutes the arguments of those who believe that in a world where all things are tossed in an infinite and endless welter of transformations, it is vain to seek a permanent basis upon abiding principles for a college curriculum.

It might also be well to encourage one starting to read the book by assuring him that the non-stop sentence derby, noticeable in the first two chapters, comes to a climax with the 55-line sentence which extends from page 27 to 29. Thereafter sentences are rarely more than a third that length.

EWING C. SCOTT

SWEET BRIAR COLLEGE
SWEET BRIAR, VIRGINIA

A LABORATORY GUIDE FOR ORGANIC CHEMISTRY. *E. Wertheim,* Professor of Organic Chemistry, University of Arkansas. Second Edition. The Blakiston Company, Philadelphia, Pa., 1940. xvi + 560 pp. 20.4 × 25.4 cm. $2.00.

The author cites that "in the preparation of this second edition the basic plan of the manual has been retained without any change."

Twenty-four additional experiments have been included: eleven preparations, four spot tests, and eight on qualitative analysis.

The manual includes a total of one hundred sixty-nine experiments, twenty-four illustrations, a table of contents, about two hundred forty pages devoted to the fill-in type report sheet, an appendix, and an index. The appendix contains special and first aid instructions, a diagrammatic representation of a series of preparations, some tables of physical data, a table of reference books, a table of atomic weights, and a list of the amounts of chemicals and reagents required for each experiment.

The manual offers a *large* variety of experiments and the time requirement is usually given, sometimes even in tabulated form. The reviewer is not convinced of the value of this feature, for he is inclined to believe that overemphasis might be placed on the quantity rather than the quality of work done.

A LABORATORY GUIDE FOR ORGANIC CHEMISTRY, a companion volume to TEXTBOOK OF ORGANIC CHEMISTRY, is imitation-leather covered, spiral bound, reasonably priced, and represents the successful accomplishment of a major undertaking.

ED. F. DEGERING

PURDUE UNIVERSITY
LAFAYETTE, INDIANA

EPHRAIM'S INORGANIC CHEMISTRY. *P. C. L. Thorne*, M.A. (Cantab.), M.Sc., Ph.D. (Lond.), F.I.C., Sometime Lecturer in Chemistry at the Sir John Cass Technical Institute, London, and at Woolwich Polytechnic, and *A. M. Ward*, Ph.D., D.Sc. (Lond.), F.I.C., Principal of the County Technical College, Guildford, Editors. Third English Edition. Nordeman Publishing Co., Inc., New York City, 1939. xii + 911 pp. 83 figs. 15.5 × 23.5 cm. $8.00.

This is one of the few outstanding advanced textbooks of inorganic chemistry. The original intention of the authors, explained in the prefaces of earlier editions, was to organize and systematize inorganic chemistry in a manner similar to that which is so well known in the field of organic chemistry. "Unconnected facts have been included only in so far as they illustrate the general matter under discussion."

The preface to this, the third English edition, explains that "this work is designed to include a great deal of information as concisely as possible and yet to present it in a palatable form. The materials of inorganic chemistry are dealt with collectively rather than individually."

The early chapters lay the fundamental groundwork upon which the later discussion is based, including such topics as: atomic and crystal structure, radioactivity, valence, the Periodic Table, isotopes, the Werner coördination theory, the parachor, allotropy, and other modifications of the elements.

The six main sections of the work are: 1, The Elements (7 chapters); 2, Halogen Compounds (6 chapters); 3, Oxides of Hydrogen and of the Metals (5 chapters); 4, The Compounds of Sulphur, Selenium, and Tellurium (3 chapters); 5, The Nitrogen, Phosphorus, Arsenic Group (5 chapters); 6, The Elements of the Fourth Group, and Boron (3 chapters). The appendix contains tables and a short section on the literature of inorganic chemistry.

The death of the author in 1935 prevented his participation in this edition. The editors are therefore responsible for the organization and revision of the book as it now stands. It fills a very important position in the chemical literature, effectively bridging the gap between the elementary textbooks and the original sources.

Despite its weighty character the book is within the grasp of the serious student, who, after having mastered it, will have a broad and comprehensive view of inorganic chemistry.

NORRIS W. RAKESTRAW

BROWN UNIVERSITY
PROVIDENCE, RHODE ISLAND

FACTORS IN THE VOCATIONAL CHOICES OF UNIVERSITY WOMEN. *G. S. M. Zorbaugh*, The Ohio State University, and *G. F. Kuder*, The University of Chicago. Edwards Brothers, Inc., Ann Arbor, Mich., 1940. v + 47 pp. 6 figs. 28 tables. 14 × 21 cm.

A critical study of the needs and the results of Vocational Counseling of Women Students of Ohio State University by means of questionnaires in 1933, 1935, 1937. The material offers a representative picture of vocational interests and accomplishments of an average group of college women students.

It shows that: (1) registration of women in professions (science, etc.) in which they are not fully welcomed by men, remains low compared to others; (2) those who decide on a vocation early in college secure better preparation, more vocational guidance, and have a greater potential value in their field; (3) vocational guidance in high school is very limited, in colleges still too much so, although a decided improvement was noted during the period studied; (4) a rather large number of students become dissatisfied in their major field before graduation (especially true in education); (5) there is a real need to help students choose their major field of interest early.

These points and others indicate definitely the need for more and better counseling, especially in fields such as chemistry where it is still difficult for a woman to succeed.

ETHEL L. FRENCH

THE UNIVERSITY OF ROCHESTER
ROCHESTER, NEW YORK

AN INTRODUCTION TO QUANTITATIVE CHEMICAL ANALYSIS. *W. C. Vosburgh*, Duke University. First Edition. Henry Holt and Co., New York City, 1941. viii + 356 pp. 27 figs. 14 × 21 cm. $2.75.

This textbook, designed "for a course of about one semester's length in which theory and practice are given about equal weight," is a modernized version of the traditional viewpoint so prevalent prior to 1920.

There are three introductory chapters, including weighing and calculations. Then come nine chapters on gravimetric methods, the first of which is general in nature. Determinations of chloride, iron, nickel, sulfate, and phosphate ions are followed by three chapters on solutions (including an exercise on specific gravity) and the theory of precipitation.

A chapter on general errors in quantitative analysis precedes the 10 chapters on volumetric methods. The latter, covering neutralization, precipitation, and oxidation-reduction reactions, contain laboratory exercises for such conventional determinations as acids and bases, and chloride, iron, and copper ions.

The succeeding chapter on voltaic cells and oxidation potentials is followed by one dealing with the literature of analytical chemistry, practical analysis, and logarithms.

The laboratory procedures include lists of the special apparatus and reagents needed. A general discussion of the process, including errors and applications, precedes the actual operating directions. At the end of nine of the 25 chapters there is a total of 116 problems, mostly of the usual type.

For a first edition this book seems very carefully done. Only a few typographical errors were noted. The conciseness and clarity of the writing is worthy of note, and the degree of accuracy of statement in the theoretical sections seems definitely higher than in certain other books in this field.

Commendable as the author's writing is, the reviewer would like to see chemical writers even more critical of their own work. Thus titrations made by weighing the titrant cannot be "volumetric" measurements. Adopting the word titrimetric for all titration methods avoids this unscientific usage and at the same time leaves the word volumetric for procedures in which the volume of a desired constituent is measured. We should distinguish more clearly between the process of measurement of a desired constituent and any operations involved in preliminary treatment of the sample or in separation of the desired constituent. Gravimetric, for example, implies a method of measurement (of mass), and as such has no essential connection with precipitation or any other method of separation. Since sampling is the analyst's first problem, its discussion on page 341 seems illogical.

M. G. MELLON

PURDUE UNIVERSITY
LAFAYETTE, INDIANA

EXPERIMENTS IN COLLOID CHEMISTRY. *E. A. Hauser*, Ph.D., Associate Professor of Chemical Engineering, and *J. E. Lynn*, Sc.D., Research Assistant in Chemical Engineering, Massachusetts Institute of Technology. First Edition. McGraw-Hill Book Company, Inc., New York City and London, 1940. xii + 178 pp. 70 figs. 15 × 23 cm. $2.00.

The authors declare that they wish to disprove a too general view that most experiments in the field of colloid chemistry are too complicated or too expensive for the average educational institution. They offer more than two hundred experiments, ranging from very simple ones of the qualitative type to a more limited number of quantitative experiments. The senior author's long experience with rubber research and with clays is drawn upon to present those subjects effectively. As stated in the Preface, "free use has been made of experiments contained in Ostwald's, Holmes', Bartell's and Hatschek's manuals."

Teachers will surely find many very workable and interesting experiments in this compact manual for their selection.

HARRY N. HOLMES

OBERLIN COLLEGE
OBERLIN, OHIO

THE CHEMICAL ACTION OF ULTRAVIOLET RAYS. *C. Ellis* and *A. A. Wells*. Revised and enlarged by *F. F. Heyroth*, M.D., Ph.D., Institute of Scientific Research, University of Cincinnati. Second Edition. Reinhold Publishing Corporation, New York City, 1941. ix + 961 pp. 159 figs. 15 × 23 cm. $12.00.

The revision by Dr. Heyroth of the earlier edition by Ellis and Wells (362 pages) has resulted in a compilation which is nearly three times the size of the original edition. Such an expansive revision is in reality a new book, using only the general outline of the original edition; a number of new subjects have been introduced as separate chapters. The book has been written so as to supply a non-mathematical explanation for the theories of radiant energy emission, absorption, and photosynthesis, and a general literature survey of the chemical action of ultra-violet rays. It will be welcomed especially by organic chemists and biochemists as well as commercial workers in fields involving photosynthesis and photo effects. There is an extensive section (270 pages) on organic chemistry, indicating the effects of ultraviolet light on organic compounds and the reactions involved. In a section of nearly the same size (220 pages) the biological applications are thoroughly discussed, this latter section being in the authors' field of specialization.

An unusually large number of references are given which make the book extremely useful as a guide to further study beyond the scope of the material presented in the text. An unusually complete author and subject index further enhances the usefulness of the book as a standard reference on the subject of the chemical action of ultra-violet rays.

WALLACE R. BRODE

OHIO STATE UNIVERSITY
COLUMBUS, OHIO

THE LIBRARY KEY, AN AID IN USING BOOKS AND LIBRARIES. *Z. Brown*, Librarian, State Teachers College, Montclair, N. J. Fourth Edition, Revised. The H. W. Wilson Company, New York City, 1940. vi + 110 pp. 17 × 25.8 cm. $0.70.

As stated in the preface, THE LIBRARY KEY is designed to instruct students in senior high schools, students in colleges, and adult readers in the use of a general library. The pamphlet may be used as a text in the course of instruction or by the individual alone. An adequate account of a typical library and its arrangement, the contents of a book with emphasis upon the methods of indexing, the card catalog, and the helpful devices used in such a compilation is presented. This is followed by a summary of the characteristics of dictionaries, encyclopedias, reference books, magazines with their classified indexes, and books, with methods for their selection. For each of these five classes a bibliography of the most important publications is listed. Any person who carefully studies this material will be able to find information of a general nature. To increase confidence in individual ability, there are sets of questions to be answered at the end of each of the chapters. When solved as problems by actual investigation, the questions give valuable experience by putting into practical use the knowledge gained by reading the KEY. The last chapters consist of a discussion of the best methods of organizing bibliographies and note-taking. The appendixes give reference books for teachers in normal schools and educators, a method to practice alphabetical arrangement, and a list of common abbreviations used by librarians in preparing their cards.

However, the reviewer is certain that except for general information this pamphlet has nothing to add to solve the specific problems of a chemist that is not given already in the well-known books on the use of chemical literature. This KEY is the type of publication that includes practically no scientific material. Therefore, the books described are not in a chemical library. The methods advocated for making records and writing references are not those adopted by the American Chemical Society publications. The KEY serves only for a general education in the use of a general library and will offer the professional chemist no additional service that his own books do not give him.

VIRGINIA BARTOW

UNIVERSITY OF ILLINOIS
URBANA, ILLINOIS

MATERIALS OF INDUSTRY. *S. F. Mersereau*, Chairman, Department of Industrial Processes, Retired, Brooklyn Technical High School. Third Edition. McGraw-Hill Book Company, Inc., New York City, 1941. xxiv + 578 pp. 246 figs. 14 × 20.5 cm. $2.00.

This textbook is designed for use especially in technical high schools and in industrial and trade schools. The author states that it aims "to give the students a working knowledge of the main facts of industry, including the distribution and production of raw materials and their general properties, transportation, conversion into commercial products, and economic importance."

The subject matter is divided into five chapters, Forest Products, Non-Metallic Minerals, Iron and Steel, Non-Ferrous Metals, Miscellaneous. Each chapter is concluded with a bibliography. The numerous subdivisions contain fairly extensive glossaries of trade and industrial terms and lists of questions graded into two levels.

It is somewhat unusual to find a textbook today with no photographs. While the use of line drawings in this case was premeditated, the attractiveness of the book would be enhanced by the use of other illustrative materials. In several instances, chemical terms have been used somewhat loosely—*e. g.*, "element" and "unite." In a few cases, more discussion is given to obsolete processes than is necessary for historical purposes. The last two chapters are somewhat less detailed than the others. These items do not seriously affect the general value of the book.

MATERIALS OF INDUSTRY was written for a specialized group of pupils at a definite age level. The author does not lose sight of that fact. He has presented a wide range of topics in a manner which should have value and appeal to the group for whom it is written. Despite the fact that this text was written for other purposes, it should be a useful reference for elementary classes in chemistry. It contains a wealth of information concerning industrial processes not usually available in the high-school library.

R. E. KEIRSTEAD

ROGERS HIGH SCHOOL
NEWPORT, RHODE ISLAND

INTRODUCTORY READINGS IN CHEMICAL AND TECHNICAL GERMAN. Edited by *J. T. Fotos*, Professor of Modern Languages, Purdue University, and *J. L. Bray*, Head of the School of Chemical and Metallurgical Engineering, Purdue University. John Wiley and Sons, Inc., New York City, 1941. xlvi + 303 pp. 13.5 × 20.5 cm. $2.50.

This, the second of a series of four texts prepared through the coöperation of the School of Chemical Engineering and the Department of Modern Languages at Purdue University, completes the publication of the series [*cf.* J. CHEM. EDUC., **15,** 247 (1938); **16,** 199–200, 306–7 (1939); **17,** 550 (1940)]. The readings are taken from Stavenhagen's "Kurzes Lehrbuch der anorganischen Chemie," Ullmann's "Enzyklopädie," Eucken and Jakob's "Der Chemie-Ingenieur" and from the journals *Stahl und Eisen* and *Metallurgie*. The book is characterized by the same features as its companion volumes. The series is planned for a four-semester course such as has been given successfully for a number of years at Purdue.

AUSTIN M. PATTERSON

ANTIOCH COLLEGE
YELLOW SPRINGS, OHIO

A STUDY OF THE PROBLEMS IN TEACHING THE SLIDE RULE. *C. N. Shuster*, Ph.D. Bureau of Publications, Teachers College, Columbia University, New York City, 1940. v + 103 pp. 20 tables. 15 × 23 cm. $1.85.

Gives new methods of teaching the slide rule, designed to cut down the number of errors in slide rule computation, with a practical exposition of the principles of approximate computation which apply. It also includes a survey of the types of problems that arise in science and industry and shows that most of them can be solved by use of the slide rule.

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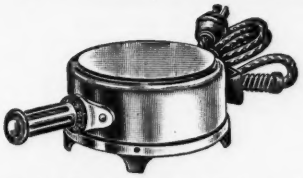

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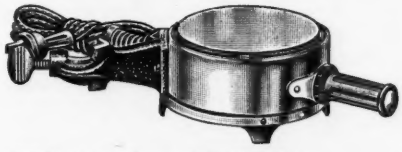

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By LUKE E. STEINER, Oberlin College. *International Chemical Series.* In press—ready for fall classes

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Following the plan of previous editions of this successful laboratory text, the present revision illustrates the principles of physical chemistry, trains the student in careful experimentation, develops familiarity with apparatus, gives him confidence in using physical chemical measurements, and encourages ability in research. While the number of experiments has not been greatly increased, much new material has been added, most of the experiments have been revised, several have been omitted, and a dozen or more new ones have been included.

Food Analysis. Typical Methods and the Interpretation of Results. *New fourth edition*

By A. G. WOODMAN, Massachusetts Institute of Technology. *International Chemical Series.* 603 pages, 6 x 9. $4.00

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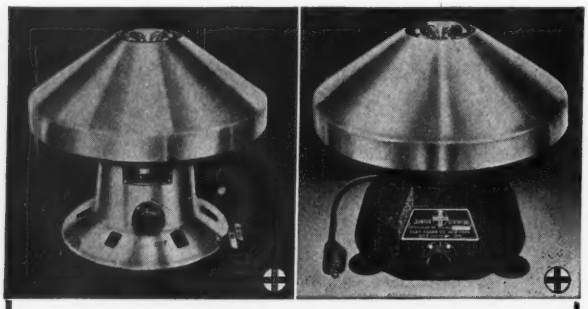

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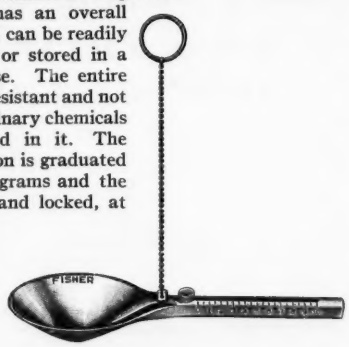

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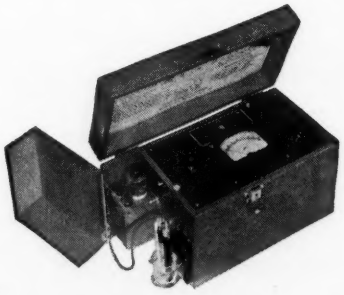

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